Talanta, 1972, Vol. 19, pp. 7 to 14. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF CALCIUM IN ZIRCONIUM POWDER BY USE OF MUREXIDE

HERMAN GORDON and GEORGE NORWITZ
Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.

(*Received* 16 *April* 1971. *Accepted* 28 *August* 1971)

Summary—An accurate spectrophotometric method is proposed for the determination of calcium in zirconium powder by use of murexide. A 0·4-g sample is dissolved in hydrofluoric and sulphuric acids, the solution evaporated to fumes of sulphuric acid, and a mercury cathode electrolysis made if more than 0·05% copper or nickel is present. Ammoniacal precipitation in the presence of ammonium chloride separates zirconium and other elements and an aliquot of filtrate is collected, equivalent to 0·2 g of sample. The ammonium salts are destroyed with nitric and hydrochloric acids and the calcium is determined with murexide. The high reagent blank is shown to be due to the reagent grade nitric acid, hydrochloric acid, and ammonium hydroxide.

ZIRCONIUM powder is used in pyrotechnics, primers, and flashlight powder. It is usually manufactured by reacting zirconium oxide or halide with calcium metal,[1,2] so calcium is a common contaminant.

There is need for an improved method for the determination of calcium in zirconium powder. The U.S. Military Specification for zirconium powder[3] describes a method in which zirconium is separated by ammoniacal precipitation, and the calcium precipitated as calcium oxalate, which is then titrated with permanganate. Elwell and Wood[4] pass a hydrofluoric acid solution of the sample through a cation-exchange resin which retains the calcium. The calcium is eluted with hydrochloric acid and determined by flame photometry or atomic absorption. The recoveries are 65–75% and the method is recommended for the determination of 0·001–0·003% calcium. The direct determination by atomic absorption is not feasible because of the quenching effect of the zirconium. Because of the lack of data, ASTM does not describe limits or methods for calcium in zirconium.[5,6]

Much work has been performed on the calcium–murexide colour and this work has been summarized by Sandell[7], by Ivanova and Simova[8] and by Hunter.[9] Surprisingly, the method does not seem to have been applied to metallic materials such as zirconium powder.

EXPERIMENTAL

Reagents

Standard calcium solutions. No. 1 (1 ml ≡ 1·0 mg Ca): dry reagent grade calcium carbonate for 3 hr in an oven at 110°, transfer 1·2486 g to a covered 400-ml beaker, add 10 ml of dilute hydrochloric acid (1 + 3), wash down the sides of the beaker, boil for 3 min, cool, and dilute to 500 ml in a volumetric flask. No. 2 (1 ml ≡ 0·01 mg Ca): dilute 5 ml of solution No. 1 to 500 ml in a volumetric flask; prepare fresh daily.

Methyl Orange indicator solution 0·1 %w/v.

Murexide solution. Dissolve 40 mg of good grade murexide in 75 ml of water at 10° in a glass-stoppered 250-ml Pyrex bottle and add 175 ml of 95% ethyl alcohol. Store in a refrigerator at about 10°. This solution will keep for at least 20 days.

Preparation of calibration curve

Rinse all glassware with hydrochloric acid before use. Transfer 2·0, 4·0, 6·0, 8·0 and 10·0-ml portions of standard solution No. 2 to 800-ml beakers and add 50 ml of water, 2 ml of sulphuric acid, 2·5 g of ammonium chloride, and 3 drops of Methyl Orange indicator. Carry a reagent blank through the entire procedure (this is essential). While swirling the beaker add ammonia solution (1 + 1) until the solution turns yellow and then add 30 ml of nitric acid. Boil down, without cover glasses, at the highest heat of the hot-plate to fumes of sulphuric acid and continue heating till complete disappearance of fumes. Allow to cool, wash down the sides of the beaker, and add 25 ml of nitric acid and 25 ml of hydrochloric acid. Again heat at highest heat of the hot-plate till complete disappearance of fumes. Allow to cool, wash down the sides of the beaker, and boil down to dryness. Again allow to cool, add 30 ml of water, and boil down to 20 ml. Cool somewhat and wash into 50-ml volumetric flasks. Cool to 10–15° in a water-bath. Remove from the water-bath, add 2·0 ml of 0·1N sodium hydroxide and wash down with a little water. Add 10·00 ml of murexide solution, dilute to the mark, and within 30 min measure the absorbance at 505 nm with a spectrophotometer that has been set to 100% transmittance with the reagent blank. (With the Beckman Model B spectrophotometer it is necessary to work with a sensitivity of about 3 in order to set the instrument to 100% transmittance.) Plot mg of calcium against absorbance.

Procedure

Transfer a 0·4-g sample to a platinum dish and add 10 ml of water, 4 ml of sulphuric acid and 2 ml of hydrofluoric acid, and swirl. Carry a reagent blank through all steps of the procedure (this is essential). Wash down the sides, evaporate to fumes of sulphuric acid at moderate heat, and fume for 2 or 3 min. Allow to cool.

If heavy metals such as copper or nickel are present in amounts greater than 0·05%, perform a mercury cathode electrolysis; otherwise proceed as in the next paragraph. For the mercury cathode electrolysis, dilute the solution to about 150 ml, wash into a mercury cathode cell, and electrolyse at 5 V for 45 min. Filter through a Whatman No. 42 filter paper into a 400-ml beaker that has graduated markings.

Dilute to about 300 ml, add 5 g of ammonium chloride and 3 drops of Methyl Orange indicator, and heat to about 90°. Remove each beaker from the hot-plate individually, add ammonia solution (1 + 1) from a burette, with vigorous stirring, until the first sign of a precipitate, and then continue the addition dropwise until the solution just becomes yellow. Dilute to the 350-ml mark with hot water (temperature about 90°) and allow the beaker to stand near the edge of the hot-plate for 5 min so that the precipitate settles. Filter immediately through a Whatman No. 41 filter paper into a 400-ml beaker with graduated markings. Discard the first 25 ml and collect 175 ml.

If the manganese content is greater than 0·05% make a manganese dioxide precipitation; otherwise proceed as in the next paragraph. To make the manganese dioxide precipitation, add 10 ml of bromine water and 5 ml of ammonia solution (1 + 1) to the 175 ml of solution in the 400-ml beaker. Digest at about 95° for 15 min, filter through a Whatman No. 42 filter paper into an 800-ml beaker, and wash with water.

Add 30 ml of nitric acid to the solution (contained in an 800-ml beaker) and proceed with the evaporations and development of the colour as described for preparation of the calibration curve. Convert the absorbance reading into mg of calcium by referring to the calibration curve. Calculate as follows:

$$\% \text{ Ca} = \frac{\text{mg of Ca as read from curve}}{\text{g of sample in aliquot} \times 10}$$

DISCUSSION AND RESULTS

Effect of temperature

The use of murexide reagent stabilized by the use of alcohol, as recommended by Williams and Moser,[10] was found to be desirable. However, the addition of a 70% alcohol solution (even if cool) caused the temperature of the sample solution to rise 4–5°, owing to the high heat of dilution of alcohol. To prevent this heating effect and subsequent instability, it is recommended that the sample solution be cooled to about 10° before addition of the water–alcohol solution of the reagent. The use of 10 ml of the reagent is recommended, since excess of murexide must be present to react with the calcium in the blank. This will be discussed later.

Effect of amount of sodium hydroxide solution

From the work of previous investigators it was judged that an alkaline medium was preferable. To ascertain the optimum amount of sodium hydroxide, various amounts of 0·1 *M* sodium hydroxide were added to solutions containing 0·05 mg of calcium. Murexide reagent (10·00 ml) was added, the solutions were diluted to 50 ml, and the transmittance was measured (after 5 and 30 min) at 505 nm against the reagent blank. The results (Table I) show that the colour intensity was essentially the same over the range 0·4–3·0 ml of 0·1 *M* sodium hydroxide. The use of 2·0 ml of 0·1 *M* sodium hydroxide is recommended (this gave a pH of 10·8 before addition of the murexide solution). The colour intensity did not change significantly over the time interval 5–30 min. The colour started to change somewhat in hue after about 1 hr.

TABLE I.—EFFECT OF AMOUNT OF 0·1*M* SODIUM HYDROXIDE (0·05 mg OF Ca PRESENT)

0·1*M* NaOH, *ml*	Transmittance, %	
	After 5 min	After 30 min
0	97	97
0·2	59	59
0·4	48	47
0·7	48	48
1·0	48	48
2·0	47	47
3·0	47	48
5·0	54	56
10·0	58	69

Absorption curves

The absorption spectrum of murexide has the absorption maximum at about 550 nm; that of calcium murexide, has the maximum at about 505 nm. It is recommended that the calcium murexide colour be read at 505 nm.

Calcium from the blank

In applying the method to zirconium, fairly large amounts of nitric acid, hydrochloric acid, and ammonia solution had to be used and it was found that these reagents contained surprisingly large amounts of calcium. The source of this calcium is probably the soft glass bottles used for shipping these reagents (bottle glass contains 4·6–14% calcium oxide[11,12]). Therefore 100-ml portions of these reagents were evaporated to dryness in platinum dishes and also Pyrex beakers. The residues were dissolved in boiling water and the calcium was determined by the murexide reaction. The results (Table II) show that on the average there were 0·025, 0·032, and 0·039 mg of calcium in 100 ml of the nitric acid, hydrochloric acid, and ammonia solution

TABLE II.—CALCIUM IN REAGENTS

Reagent	Calcium found, *mg/100 ml*	
	Evaporated in platinum	Evaporated in Pyrex
Nitric acid	0·027	0·023
Hydrochloric acid	0·031	0·032
Ammonium hydroxide	0·040	0·038

respectively. The results did not differ significantly for samples evaporated in platinum dishes or Pyrex beakers (this was not unexpected, since Pyrex does not contain detectable amounts of calcium[13]).

Equilibrium conditions for the calcium murexide complex depend somewhat on the amount of calcium present. Hence, in preparing the calibration curve it is necessary to treat portions of standard calcium solution with nitric acid, hydrochloric acid, and ammonia solution as in the method, in order to compensate for the effect of the large amount of calcium contained in these reagents.

The blank from these materials could be reduced by use of specially purified reagents. However, this laboratory was interested in methods that would use ordinary analytical reagents.

Study of separations

The cupferron precipitation followed by chloroform extraction was ruled out because it did not eliminate several interfering metals. Ion-exchange was found to be open to the same objections. The separations finally decided upon were a mercury cathode electrolysis, followed by an ammoniacal precipitation in the presence of ammonium chloride to provide buffering.[13] It is known that zirconium and calcium hydroxides are precipitated at pH 3 and 12·5 respectively.[13] To avoid washing the precipitate a fraction of the hot filtrate is taken. This is readily done by using beakers with graduated markings. There is a small error caused by expansion, but because the fraction used is very large and the amount of calcium in zirconium is small (less than 0·05%), the error is not significant.

An important advantage of the use of the ammoniacal precipitation is that the zirconium hydroxide acts as scavenger to remove many possible interfering metals from solution. It would be expected that small or moderate amounts of the following would be completely co-precipitated with zirconium hydroxide: hafnium, titanium, chromium, vanadium, uranium, aluminium, iron, phosphorus, lead, bismuth, tin, arsenic, antimony, selenium, tellurium, gallium, germanium, niobium, tantalum, beryllium, cerium, thorium, indium, and platinum metals.

After the ammoniacal precipitation it was necessary to destroy the large amount of ammonium salts before the colour could be developed. Initially, this was done by evaporating the filtrate to dryness in a platinum dish and heating over an open flame to volatilize the ammonium chloride and ammonium sulphate. It was found that considerable calcium was lost in the cloud of vapours, so this technique was abandoned. The method finally adopted was the nitric–hydrochloric acid treatment to oxidize the ammonium ion to nitrogen. No ammonium salts remained after this treatment and no calcium was lost. The technique is fairly rapid since the evaporations are conducted at the highest heat of the hot-plate.

Study of interferences

The use of both the mercury cathode electrolysis and ammoniacal precipitation eliminates all except a few elements. Manganese and tungsten are partially removed, while calcium, sodium, potassium, lithium, magnesium, barium and strontium are not removed. Potassium and lithium are not found in zirconium. Sodium is occasionally found in traces in zirconium but does not interfere (the hydroxide is used in the procedure). The investigation of interferences was therefore confined to magnesium, barium, strontium, manganese, tungsten and mercury (possible contamination from the mercury cathode).

The results are shown in Table III. These indicate that there is a complex equilibrium involving calcium, the second metal and murexide. The following are suggested as the maximum permissible limits (per 50 ml) for the interfering ions: magnesium, 0·3 mg; barium, 0·2 mg; strontium, 0·01 mg; manganese, 0·1 mg; tungsten, 1 mg; mercury, 0·2 mg.

Williams and Moser,[10] using pH 11·2 and a different technique, found that the maximum permissible amounts of magnesium, barium, and strontium were 0·5, 0·25, and 0·05 mg per 50 ml, respectively.

TABLE III.—STUDY OF INTERFERENCES

Interfering element, *mg*		Calcium present, *mg*	Calcium found, *mg*
Mg	0·1	0·000	0·000
	0·3	0·000	0·000
	0·5	0·000	0·008
	1·0	0·000	0·016
	1·5	0·000	0·044 (amber)
	0·2	0·050	0·049
	0·5	0·050	0·049
	1·0	0·050	0·048
	1·5	0·050	0·054
Ba	0·05	0·000	0·000
	0·01	0·000	0·000
	0·2	0·000	0·001
	0·3	0·000	0·003
	0·5	0·000	0·003
	1·0	0·000	0·007
	0·1	0·050	0·052
	0·3	0·050	0·062
	0·5	0·050	0·062
	1·0	0·050	0·065
Sr	0·01	0·000	0·002
	0·05	0 000	0·008
	0·1	0·000	0·028
	0·3	0·000	0·060
	0·5	0·000	0·072
	0·1	0·050	0·072
	0·3	0·050	0·106

TABLE III (*continued*)

Interfering element, *mg*		Calcium present, *mg*	Calcium found, *mg*
Mn	0·05	0·000	0·000
	0·1	0·000	0·002
	0·3	0·000	0·006
	0·5	0·000	0·010
	1·0	0·000	0·108 (amber)
	0·05	0·050	0·047
	0·1	0·050	0·049
	0·3	0·050	0·049
	0·5	0·050	0·048
	1·0	0·050	0·125 (amber)
W	0·1	0·000	0·000
	0·5	0·000	0·000
	20·0	0·000	0·000
	30·0	0·000	0·002
	0·3	0·050	0·053
	1·0	0·050	0·049
	2·0	0·050	0·036
	10·0	0·050	0·000
Hg(II)	0·1	0·000	0·000
	0·3	0·000	0·000
	0·5	0·000	0·006
	1·0	0·000	0·032
	3·0	0·000	0·049
	0·1	0·050	0·050
	0·3	0·050	0·054
	0·5	0·050	0·056
	1·0	0·050	0·075

The recommended interference limits would indicate that the proposed method would be applicable to samples (0·2 g aliquot) containing less than 0·15% magnesium, 0·1% barium, 0·005% strontium, 0·05% manganese, and 0·5% tungsten. These amounts of magnesium, barium, strontium, and tungsten are less than the amounts to be found in commercial zirconium powder. It is rare for a sample of zirconium powder to contain more than 0·05% manganese. However, to take care of all eventualities, it was decided to include a precipitation of the manganese dioxide,[14] when the manganese content is appreciable. Some of the manganese would, of course, be deposited at the mercury cathode. The maximum permissible amount of mercury is more than that which would be found in the solution after the electrolysis.

Results for calcium in zirconium powder

The results obtained for calcium in four samples of zirconium powder are shown in Table IV. The samples contained 0·000–0·042% calcium. Good recoveries were obtained on adding standard calcium solution to samples of calcium-free zirconium and carrying these synthetic samples through the procedure (Table V).

TABLE IV.—RESULTS FOR CALCIUM IN ZIRCONIUM POWDER

Sample	Calcium found, %
1*	0·007, 0·006, 0·008
2*	0·004, 0·005
3*	0·000, 0·000
4	0·011, 0·009
5 (granular, low grade)†	0·039, 0·042

* Mercury cathode electrolysis omitted.
† Contains 0·10% manganese.

TABLE V.—RECOVERY OF CALCIUM FROM SYNTHETIC SAMPLES

Synthetic sample	Calcium recovered, *mg*
0·4 g of sample 3 + 0·025 mg of calcium	0·026
0·4 g of sample 3 + 0·050 mg of calcium	0·049
0·4 g of sample 3 + 0·100 mg of calcium	0·097

Zusammenfassung—Eine genaue spektrophotometrische Methode zur Bestimmung von Calcium in Zirkoniumpulver mittels Murexid wird vorgeschlagen. Eine Probe von 0,4 g wird in Flußsäure und Schwefelsäure gelöst, die Lösung bis zum Rauchen der Schwefelsäure eingedampft und, falls mehr als 0,05% Kupfer oder Nickel vorliegen, an einer Quecksilberkathode elektrolysiert. Eine Ammoniakfällung in Gegenwart von Ammoniumchlorid trennt Zirkonium und andere Elemente ab. Ein 0,2 g Probe entsprechender aliquoter Teil des Filtrats wird gesammelt, die Ammoniumsalze mit Salpetersäure und Salsäure beseitigt und das Calcium mit Murexid bestimmt. Es wird gezeigt, daß der hohe Blindwert von der analysenreinen Salpetersäure und Salzsäure sowie vom Ammoniumhydroxid herrührt.

Résumé—On propose une méthode spectrophotométrique précise pour le dosage du calcium dans la poudre de zirconium au moyen de murexide. On dissout un échantillon de 0,4 g dans les acides fluorhydrique et sulfurique, évapore la solution jusqu'à apparition des fumées d'acide sulfurique, et effectue une électrolyse à cathode de mercure s'il y a plus de 0,05% de cuivre ou de nickel. La précipitation ammoniacale en présence de chlorure d'ammonium sépare le zirconium et les autres éléments, et l'on recueille une partie aliquote du filtrat, équivalant à 0,2 g d'échantillon. Les sels d'ammonium sont détruits aux acides nitrique et chlorhydrique et l'on dose le calcium avec le murexide. On montre que la valeur élevée du témoin des réactifs est due à la qualité de l'acide nitrique, de l'acide chlorhydrique et de l'ammoniaque.

REFERENCES

1. H. C. Anderson and L. H. Belz, *J. Electrochem. Soc.*, 1953, **100**, 240.
2. G. L. Miller, *Metallurgy of the Rarer Metals, Vol. 2, Zirconium*, pp. 122, 482. Academic Press, New York, 1957.
3. *Military Specification MIL-Z-399C, Zirconium Powder*, February 1969.
4. W. T. Elwell and D. F. Wood, *Analysis of the New Metals*, pp. 19, 145. Pergamon Press, New York, 1966.
5. *1970 Annual Book of ASTM Standards, Part 7, Non-ferrous Metals and Alloys; Electrodeposited Metallic Coatings; Metal Powders*, Designations B 350-65, B 351-67, B 352-67, B 353-69, B 356-67. ASTM, Philadelphia.
6. *1970 Annual Book of ASTM Standards, Part 32, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores*, Designation E 146-68. ASTM, Philadelphia.

7. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, pp. 368, 380. Interscience, New York, 1959.
8. F. Ivanova and L. Simova, *Rudodubiv Met.* (*Sofia*), 1967, **22**, 44.
9. G. Hunter, *Analyst*, 1959, **84**, 24.
10. M. B. Williams and J. H. Moser, *Anal. Chem.*, 1953, **25**, 1414.
11. G. W. Morey, *Properties of Glass*, p. 76. Reinhold, New York, 1954.
12. S. R. Scholes, *Modern Glass Practice*, p. 42. Industrial Publications, Chicago, 1941.
13. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, pp. 18, 76, 501. Wiley, New York, 1953.
14. *1970 Annual Book of ASTM Standards, Part 32, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores*, Designation E 34-68, par. 84.1.4. ASTM, Philadelphia.

Talanta, 1972, Vol. 19, pp. 15 to 19. Pergamon Press. Printed in Northern Ireland

MICRODOSAGE DU SILICIUM DANS LES COMPOSES ORGANIQUES*

E. Debal
(avec la collaboration technique de M. Riocreux)
Service Central de Microanalyse du Centre National de la Recherche Scientifique, 2, rue Henry Dunant, 94–Thiais, France

(*Reçu le* 28 *juin* 1971. *Accepté le* 23 *août* 1971)

Résumé—Les composés organiques siliciés sont minéralisés en bombe de Würzschmitt par le peroxyde de sodium et le silicate formé est dosé par spectrophotométrie de l'ion silicomolybdique. La masse du prélèvement analytique varie de 2 à 6 mg. L'erreur absolue possible sur la teneur en silicium est de 0,3–0,4%.

Le microdosage du silicium à l'échelle microanalytique a donné lieu à quelques travaux dont Reverchon et Legrand[1] ont fait un bref rappel.

Minéralisation

En outre, Klimova et collaborateurs,[2] puis Klimova et Bereznitskaya,[3] Shostakovskii et collaborateurs,[4] Gel'man,[5] ont décrit des méthodes permettant les dosages simultanés du silicium, du carbone et de l'hydrogène, par combustion sous courant d'oxygène, comportant le pesage de la silice formée qui reste à l'intérieur de la cartouche en quartz où a brûlé le prélèvement analytique. Leur application n'a pas paru appropriée aux besoins de notre Service qui requéraient une méthode plus spécifique se prêtant mieux à une mise en oeuvre sporadique.

La méthode de calcination en creuset de platine en présence d'acide sulfurique (Ridge et Todd cités par Belcher[6]) avec dosage gravimétrique de la silice, mise en oeuvre à l'échelle milligrammique pendant quelques temps dans notre Service, malgré son défaut de spécificité, y a été abandonnée. Elle conduit en effet trop souvent à des erreurs systématiques portant sur plusieurs microgrammes de silicium et, en outre, elle ne convient pas à l'analyse de la plupart des substances liquides. De telles difficultés avaient d'ailleurs été déjà signalées notamment par Belcher[6] ainsi que par Brown et Fowles,[7] ces derniers effectuant une attaque initiale du prélèvement analytique par un mélange d'acide sulfurique et d'acide nitrique.

La méthode de minéralisation par combustion en fiole de Schöniger a été adoptée par quelques microanalystes tels que Burroughs[8] qui utilise une fiole en polyéthylène et Reverchon et Legrand[1] qui emploient une fiole en nickel.

Les quelques essais que nous avons effectués avec minéralisation en fiole de polypropylène (marque "Nalgène") dont nous disposions n'ont pas été encourageants: ils ont conduit à l'obtention de résultats erronés par défaut et à la perforation fréquente des fioles, par combustion, lorsque des particules enflammées viennent au contact de leur paroi de matière plastique. La fiole de nickel ne présente pas ce dernier inconvénient mais son opacité ne se prête pas non plus à un allumage simple en son sein. Ces essais ont donc été abandonnés au profit de l'étude de la minéralisation en bombe par le peroxyde de sodium à l'instar de quelques

---

* Communication présentée dans le cadre des Journées de microanalyses organisées par la Société Chimique de France et la Société de Chimie Industrielle, à Thiais, les 18 et 19 mars 1971.

microanalystes tels que Christopher et Fennell[9] qui utilisent 0,2 g de ce réactif et portent leur bombe à 500° pendant 15 min.

La méthode décrite ci-après est une variante de la méthode initiale de Würzschmitt.[10] Elle est associée à l'utilisation des sachets de "Scotch" décrits par Reverchon[1] pour le conditionnement, le pesage et l'attaque du prélèvement analytique dans la bombe; non seulement ces sachets sont indispensables dans le cas de la minéralisation de produits liquides mais, de plus, ils semblent faciliter la minéralisation de certaines substances solides dont les résultats d'analyse sont erronés par défaut lorsque les prélèvements analytiques sont déposés directement au fond de la bombe à l'aide d'un pèse-substance d'après le mode opératoire original de Würzschmitt.

Dosage

Le silicate formé est dosé par colorimétrie spectrophotométrique du complexe jaune silicomolybdique utilisé par de nombreux analystes tels que Reverchon.[1]

Cependant il n'est pas établi de courbes d'étalonnage; il est préférable de préparer des solutions étalons en même temps que les solutions inconnues qui leur sont directement comparées, comme nous l'avons indiqué par ailleurs.[11] Les calculs sont fondés sur l'application d'une simple règle de proportionnalité. En vue d'améliorer la précision, la loi de Lambert-Beer n'étant pas rigoureusement suivie dans les conditions opératoires décrites, les teneurs en silicium des solutions étalons doivent être voisines de celles des solutions à titrer (les écarts admissibles entre ces teneurs ne doivent pas excéder 60–80 μg de silicium par fiole jaugée de 200 ml).

Il est connu que le complexe silico-12-molybdique existe sous deux formes α et β, dont la seconde a un coefficient d'extinction double de celui de la première à $\lambda \sim 400$ nm et se transforme lentement et irreversiblement en forme α. Lorsqu'on effectue la mesure de densité optique une quinzaine de minutes après l'addition du molybdate, comme il est en général indiqué dans la littérature, le complexe existe alors, en principe, sous la forme β mais d'après Strickland cité par Hargis[12] il est impossible d'obtenir une solution d'isomère β seul. Nous avons effectué des séries de mesures de densités optiques 15 min, 45 min et 17 hr après l'addition de molybdate d'ammonium. Elles nous ont montré que les quantités de silicium trouvées sont en général très voisines dans le cas des mesures effectuées après 15 ou 45 min c'est à dire, sur le complexe β, en principe, mais que par contre elles sont quelquefois légèrement différentes au bout de 15 à 18 hr, c'est à dire sur le complexe α. Ce sont les dosages effectués sur le complexe α qui sont les plus exacts. Comme la quantité de peroxyde de sodium utilisée est définie à 0,1–0,2 g près, il s'en ensuit que le pH peut varier légèrement d'une fiole à l'autre puisque la quantité d'acide ajoutée est constante. Or la valeur du pH joue un rôle important dans la formation des complexes α et β; il est donc possible qu'après addition du molybdate d'ammonium, il se forme immédiatement des quantités faibles mais variables de complexe α ce qui expliquerait la meilleure reproductibilité des résultats lorsque l'ion silicomolybdique est entièrement sous la forme α, c'est à dire après 16 à 18 hr d'attente.

PARTIE EXPERIMENTLLE

Materiel

Microbombes de Würzschmitt en nickel avec joint de Téflon[13] et dispositif de chauffage et de protection.

Spectrophotomètre "graphi-spectral" Jouan à 2 cuves, sans enregistreur.
Béchers de 150 ml en Téflon.
Accessoires divers: pipettes de précision, bain de sable, fioles jaugées de précision de 200 ml.

Reactifs

Glycol éthylénique pour usages scientifiques.
Peroxyde de sodium en poudre pour analyses.
"Scotch" Minnesota en ruban de 19 mm de largeur.
Acide sulfurique ($d = 1{,}83$) pour analyses. Diluer pour obtenir de l'acide 7*N*.

Solution de molybdate d'ammonium. Dissoudre 106 g de molybdate d'ammonium, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, pour analyses, dans de l'eau distillée. Ajuster le pH à 7–7,5 en ajoutant environ 28 g de soude en pastilles pour analyses et en diluant à 1 litre avec de l'eau distillée. Conserver la solution en flacon de polyéthylène.

Solutions de silicate de sodium à 40 et 100 mg de silicium par litre (variante de la méthode de Reverchon[1]). Introduire soit 85,60 mg (solution à 40 mg/l), soit 214,00 mg (solution à 100 mg/l) de silice exempte de carbone, pour analyses métallurgiques, dans une capsule de platine. Ajouter soit environ 6 g (solution à 40 mg/l), soit environ 12 g (solution à 100 mg/l) de soude en pastilles pour analyses. Faire fondre en chauffant doucement, maintenir le chauffage pendant 30 min et après refroidissement reprendre par de l'eau distillée bouillante. Ajuster le pH à 1,5 (essai à la touche sur papier à pH) en ajoutant de l'acide sulfurique 7*N* (environ 20 ou 40 ml) et en diluant à 1 litre avec de l'eau distillée. Transvaser immédiatement dans un flacon en polyéthylène.

Mode opératoire

Préparer des sachets de "Scotch" revêtus intérieurement de papier filtre sans cendres analogues à ceux de Reverchon[1] mais d'environ 10 mm de hauteur totale et sans languette. Peser dans chacun de ces sachets 2 à 6 mg de substance de telle sorte que la masse de silicium y soit, si possible au plus égale à 0,7 mg.* Lors de l'analyse de substances liquides, introduire au préalable dans chaque sachet quelques carrés de papier filtre sans cendres d'environ 2 mm de côté et déposer le liquide sur le papier à l'aide d'une tige capillaire. Effectuer la minéralisation à l'aide de 2,6 g de peroxyde de sodium en présence de 2 à 3 gouttes d'éthylène-glycol selon la méthode de Würzschmitt.[10]

Après minéralisation et refroidissement, préparer, pour chaque bombe, un bécher de Téflon contenant un petit carré de toile de platine (36 mailles par mm^2) destiné à catalyser la décomposition ultérieure de l'eau oxygénée formée par dissolution dans l'eau du peroxyde de sodium. Introduire chaque bombe dans un bécher de Téflon; rincer le couvercle de la bombe à l'eau distillée bouillante et recueillir l'eau de rinçage dans le bécher; y ajouter de l'eau distillée bouillante jusqu'à ce que le corps de la bombe soit juste recouvert, ce qui donne lieu à la dissolution de la masse d'attaque. Couvrir le bécher avec un "verre de montre" en Téflon et le poser sur un bain de sable à 200° en vue de détruire l'eau oxygénée. Au bout de 45 min, rincer le "verre de montre", extraire le corps de la bombe et le rincer avec de l'eau distillée bouillante; recueillir toutes les eaux de rinçage dans le bécher. Ajouter lentement 9,5 ml d'acide sulfurique 7*N* pour que la solution soit portée à un pH voisin de 1,5 et laisser revenir à température ambiante. Transvaser la solution, en la filtrant sur papier filtre sans cendres à filtration rapide, dans une fiole jaugée de 200 ml préalablement garnie de 5,7 ml d'acide sulfurique 7*N* de telle sorte que le pH final reste égal à 1,5. On obtient ainsi une série de fioles correspondant à la série de prélèvements analytiques et de minéralisations effectués. Préparer en même temps des solutions étalons et un essai à blanc suivant le même mode opératoire mais en introduisant un sachet de "Scotch" vide dans chaque bombe puis *n* ml de solution de silicate de sodium dans la fiole jaugée correspondante avec $n = 0$ dans le cas de l'essai à blanc. Ajouter dans chacune des fioles 20 ml de solution de molybdate d'ammonium et ajuster le volume de la solution à 200 ml avec de l'eau distillée.

Effectuer la mesure spectrophotométrique par rapport à l'essai à blanc à 400 nm après 15 à 18 h de repos.

Calcul

Soit *d* la densité optique d'une solution inconnue, D, D', D'', D''' les densités optiques de 4 solutions étalons identiques correspondantes

$$\text{Si}\ \% = \frac{d \times m' \times 100}{\dfrac{D + D' + D'' + D'''}{4} \times m}$$

* Lorsque la masse croît au delà de 0,7 mg, la précision diminue souvent peu à peu.

m': masse de silicium introduite dans chaque solution étalon, exprimée en mg; m: masse du prélèvement analytique exprimée en mg.

(Pour 0,5 mg de silicium, d est de l'ordre de 0,24)

DISCUSSION

La méthode décrite est de longue durée et délicate à mettre en oeuvre par suite des nombreuses manipulations qu'elle comporte et de la perturbation susceptible d'être apportée par l'eau oxygénée au cas où celle-ci ne serait pas quantitativement détruite. Il est donc important que cette destruction soit opérée dans des conditions rigoureusement reproductibles pour toutes les solutions, que, par conséquent, les volumes de solutions à porter à l'ébullition soient les mêmes et que la température du bain de sable soit uniforme. Du fait de l'existence de ces différentes causes d'erreurs, il est recommandé de préparer simultanément 4 solutions étalons identiques afin de pouvoir éventuellement éliminer le résultat fourni par l'une d'elles s'il apparaît que celui-ci est manifestement erroné.

Afin de réduire au minimum le temps passé, grouper les substances par teneurs afin que la moyenne des résultats obtenus pour ces 3 ou 4 solutions étalons soit utilisable pour le calcul de la teneur en silicium de plusieurs substances soumises à l'analyse (les quantités de silicium à doser ne doivent pas différer de plus de 60 à 80 μg: *cf. Dosage*).

RESULTATS

Quelques exemples de résultats de microdosages du silicium sont reportés dans le Tableau I. Ils mettent en évidence l'exactitude et la reproductibilité que peut fournir

Tableau I.—Exemples de résultats de microdosage du silicium

Composé	Prélèvement analytique, *mg*	Teneur en silicium, %	
		Trouvée	Calculée
Triphénylsilanol	5,978	$10{,}3_0$	10,16
	5,717	$10{,}2_4$	—
	5,289	$10{,}2_1$	—
	5,269	$10{,}1_7$	—
	4,262	$9{,}9_0$	—
	5,891	$10{,}0_3$	—
	4,208	$10{,}0_8$	—
	5,275	$10{,}0_5$	—
	3,097	$10{,}2_6$	—
	3,214	$9{,}8_0$	—
	5,727	$10{,}4_1$	—
	4,164	$10{,}3_5$	—
Triphénylsilane	5,472	$10{,}9_5$	10,79
	3,646	$10{,}6_4$	—
	4,919	$10{,}8_7$	—
	3,950	$10{,}5_3$	—
	4,019	$10{,}8_7$	—
	5,455	$10{,}9_6$	—
	5,356	$10{,}4_8$	—
Composé de recherche A (liquide)	5,165	$9{,}2_7$	9,33
	5,231	$9{,}3_1$	—
Composé de recherche B (liquide)	4,300	$11{,}4_4$	11,22
	4,486	$11{,}3_5$	—
Composé de recherche C	3,493	$18{,}2_1$	17,97
	3,721	$18{,}1_0$	—

la méthode décrite. L'écart type estimé calculé d'après la formule classique

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n - 1}}$$

a pour valeur $s = 0{,}17$ Si % pour l'ensemble des résultats, ce qui correspond encore à une erreur possible atteignant au plus 0,3–0,4 Si %.

Summary—Organic silicon compounds are decomposed by sodium peroxide in a Würzschmitt nickel bomb. The silicate obtained is determined spectrophotometrically as silicomolybdate. The sample weight is 2–6 mg. The possible absolute error in the silicon content is 0·3–0·4%

Zusammenfassung—Organische Siliciumverbindungen werden mit Natriumperoxid in einer Nickelbombe nach Wurzschmitt aufgeschlossen. Das erhaltene Silikat wird spektrophotometrisch als Silikomolybdat bestimmt. Das Probengewicht beträgt 2–6 mg, der mögliche Absolutfehler im Siliciumgehalt 0·3–0·4%.

BIBLIOGRAPHIE

1. R. Reverchon et Y. Legrand, *Chim. Anal.*, 1965, **47**, 194.
2. V. A. Klimova, M. O. Korshun et E. G. Bereznitskaya, *Dokl. Akad. Nauk SSSR*, 1952, **84**, 1175; 1954, **96**, 81; *Zh. Analit. Khim.*, 1956, **11**, 223.
3. V. A. Klimova et E. G. Bereznitskaya, *Zh. Analit. Khim.*, 1956, **11**, 292.
4. M. F. Shostakovskii, V. I. Skorobogatova, Yu. M. Faershtein, L. V. Balashenko et G. V. Parshakova, *ibid.*, 1968, **23**, 754.
5. N. E. Gel'man, *Talanta*, 1967, **14**, 1423.
6. R. Belcher, D. Gibbons et A. Sykes, *Mikrochemie*, 1952, **40**, 76.
7. M. P. Brown et G. W. Fowles, *Anal. Chem.*, 1958, **30**, 1689.
8. J. E. Burroughs, W. G. Kator et A. I. Attia, *ibid.*, 1968, **40**, 657.
9. A. J. Christopher et T. R. F. W. Fennell, *Talanta*, 1965, **12**, 1003.
10. B. Würzschmitt, *Chem. Ztg.*, 1950, **74**, 356; *Mikrochem. Mikrochim. Acta*, 1951, **36–37**, 769.
11. E. Debal, *Chim. Anal.*, 1963, **45**, 66.
12. L. G. Hargis, *Anal. Chim. Acta*, 1970, **52**, 1.
13. R. Levy, *Monographies de Chimie Organique*, Vol. IV, *Microanalyse organique élémentaire qualitative et quantitative*, p. 144. Masson, Paris, 1961.

Talanta, 1972, Vol. 19, pp. 21 to 29. Pergamon Press. Printed in Northern Ireland

FLUORIMETRIC AND PHOSPHORIMETRIC CHARACTERISTICS OF SEVERAL VITAMINS*

JEAN-JACQUES AARON† and J. D. WINEFORDNER®
Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.

(*Received* 10 *May* 1971. *Accepted* 18 *August* 1971)

Summary—The fluorescence and phosphorescence characteristics of 14 vitamins were evaluated. The existence or absence of fluorescence and phosphorescence was compared with predictions based upon molecular structure. Analytically useful fluorescence signals were obtained for *p*-aminobenzoic acid, folic acid, calciferol, pyridoxine hydrochloride, riboflavine, α-tocopherol and vitamin A, whereas analytically useful phosphorescence signals were obtained for *p*-aminobenzoic acid, folic acid, niacinamide, pyridoxine hydrochloride, and α-tocopherol. All other vitamins either did not fluoresce or phosphoresce or could not be measured, owing to experimental difficulties. The complementary nature of fluorimetry and phosphorimetry is evident in these studies.

NUMEROUS fluorimetric assays have been developed for vitamins.[1] Most of these studies have involved measurement of fluorescence characteristics, study of pH and solvent effects upon fluorescence signals and spectra, and development of extraction procedures for separation of vitamins from biological fluids and conversion of vitamins into fluorescent compounds.[1] In contrast to the rather extensive fluorescence studies, the knowledge of the phosphorescence characteristics of vitamins is quite limited, and, at present, no use of phosphorimetry[2–4] for analysis of vitamins has been reported. The lack of use of phosphorimetry for studies involving biological samples was impeded, until recently, by the difficulty of sample cell alignment and the need for organic solvents which would form clear, rigid glasses at liquid nitrogen temperatures; as a result of the rotating sample-cell assembly described by Zweidinger and Winefordner,[5] the previous problems have been minimized, and phosphorimetry is now capable of analytical use for measurement of trace species in biological samples.

The purpose of the present research was to evaluate the fluorescence and phosphorescence characteristics of 14 vitamins and to compare the usefulness of fluorimetry and phosphorimetry for quantitative analysis of these compounds.

EXPERIMENTAL

Instrumentation

Fluorescence measurements were performed with either a Baird Fluorispec (Model SF-100; Baird Atomic Inc., Bedford, Mass.) or an Aminco-Bowman SPF (Model 4-8202, American Instrument Co., Inc., Silver Spring, Md.) spectrophotofluorimeter. A 150 W Hanovia d.c. power supply was used to power the xenon arc lamp with the Baird unit, whereas a Harrison (Model 6268A, Hewlett-Packard, Palo Alto, Calif.) constant current d.c. power supply was used to power the xenon arc lamp with the Aminco unit. All spectra were recorded with an X-Y recorder.

Phosphorescence measurements were performed by using the Aminco-Bowman SPF with an Aminco-Keirs phosphoroscope attachment (Model, C27-62140, American Instrument Co., Inc.) and the rotating sample-cell described by Zweidinger and Winefordner.[5] Phototube signals were measured

---

* Research carried out as a part of a study on the phosphorimetric analysis of drugs in blood and urine, supported by U.S. Public Health Service Grant (GM 11373-08).

† On leave from Laboratoire de Chimie Organique Physique, Paris, France.

by using the low noise nanoammeter described by O'Haver and Winefordner.[6] The stable Harrison power supply used for fluorescence studies was also used to power the 150-W xenon arc source.

Reagents

All vitamins studied here were purchased as a kit (Nutritional Biochemicals Corp., Cleveland, Ohio) and used as received. Solvents used were ethanol which was purified by distillation through a 1·5-m vacuum-jacketed column,[7] and demineralized water.

Procedure

Stock ethanolic solutions of all vitamins, except for inositol, calcium pantothenate, and riboflavin, which had to be prepared in water, were prepared. Inositol and calcium pantothenate are insoluble in ethanol, and riboflavin is known[8] to photolyse much faster in ethanolic than aqueous solutions. Lower concentrations of each vitamin were prepared by successive dilutions.

The spectrometric slit arrangements for fluorimetry were: 4, 1, 1, 3, 3, 3 for the Aminco instrument; and 1, 1, 1, 1 for the Baird instrument. The spectrometric slit arrangements for phosphorimetry were: 4, 3, 3, 3, 3, 3. The numbers refer to the slit dimensions (mm) and the sequence refers to the manufacturer's means of specifying slits within the spectrometric instrument. All excitation and emission spectra, analytical curves, and detection limits were obtained (for a given instrument) with the same slit arrangement. All spectra were uncorrected for instrumental response.

RESULTS AND DISCUSSION

Fluorescence and phosphorescence excitation and emission spectra

Eight of the 14 vitamins fluoresced or phosphoresced or exhibited both fluorescence and phosphorescence; the measured fluorescence and phosphorescence spectral characteristics of these eight are given in Table I. The reported fluorescence and phosphorescence characteristics of the parent compounds are also given in Table I for comparison. Six compounds, including ascorbic acid, biotin, calcium pantothenate, thiamine hydrochloride, inositol and choline chloride did not fluoresce or phosphoresce with sufficient intensity to be of analytical use.

The main reasons for the occurrence (or lack) of fluorescence and phosphorescence of vitamins may be attributed to the great variety of structures and to dissociation energy considerations.[9] It is well known that the existence of a conjugated system in the molecule is necessary for fluorescence because π–π^* singlet states are preferred; on the other hand, aromatic hydrocarbons, heterocycles, and carbonyl compounds involving n–π^* or π–π^* triplet states undergo phosphorescence. Vitamins (see Table II) usually contain several of these structural features. From the information in Table II, it would seem that all but 2 vitamins should fluoresce and/or phosphoresce. From the results in Table I, there are some cases of disagreement between predicted and observed fluorescence and phosphorescence. These might be a result of either particular geometrical arrangements of the molecule or a result of predissociation.

In Table III, the absorption maxima (in kJ/mole) of the vitamins with the bond dissociation energy (in kJ/mole) of their weakest bond are compared. The data show that generally the vitamins fluoresce only when they absorb at lower-energy frequencies than the dissociation energy of their least stable bond; under these conditions, there should be no predissociation and the vitamins are able to fluoresce. Niacinamide and thiamine hydrochloride (both were predicted to fluoresce, from their structural characteristics, but did not fluoresce experimentally—see Table II) have very much higher absorption energies (in kJ/mole) than the dissociation energies of their weakest bond and, therefore, they are probably predissociated and unable to fluoresce.

The fluorescence and phosphorescence bands of vitamins are generally broad and

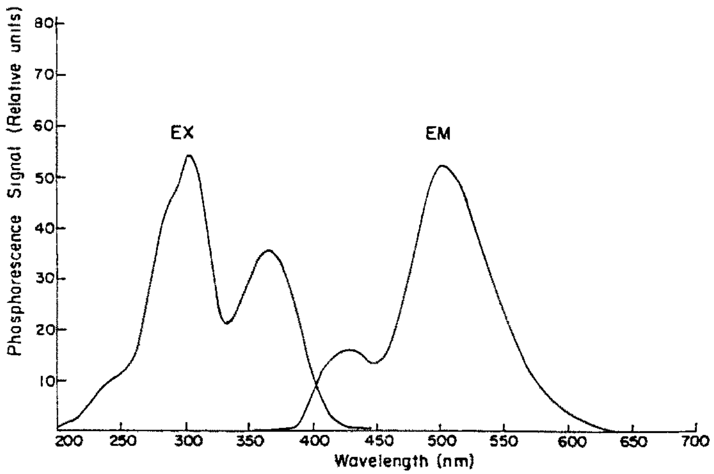


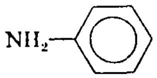
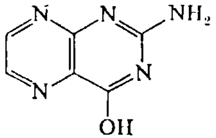
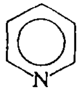
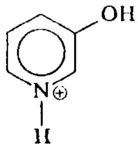
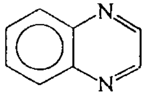
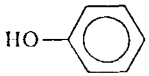
FIG. 1.—Phosphorescence excitation and emission spectra of folic acid in ethanol (77K).

structureless. In some cases, the excitation or the emission spectra exhibit several peaks. For instance, the phosphorescence excitation and emission spectra of folic acid include two peaks each (Fig. 1): the emission peak at 425 nm is attributed to the anilino part of the folic acid and the emission peak at 505 nm is related to the pteridin part of the molecule, as can be seen by comparing these wavelength values with those of the parent compounds (see Table I). Generally, the spectra of the vitamins resemble those of the parent compounds very closely (see Table I). However, in some cases, such as pyridoxine hydrochloride and α-tocopherol, a red shift of the fluorescence and phosphorescence bands is observed relative to the parent compound (Table I); this shift may be attributed to the effect of electron-donating alkyl and alkoxy substituents. In the case of the niacinamide, the parent compound pyridine does not phosphoresce, but the vitamin phosphoresces; the appearance of the phosphorescence is related to the substitution of the carbonyl group in the pyridine ring, which is known to favour the appearance of phosphorescence.[11]

Analytical studies

Fluorescence and phosphorescence analytical characteristics are given in Table IV. The linear portion of the analytical curves was much the same whether measured with the Aminco-Bowman or the Fluorispec instrument. The limit of detection was taken as the concentration giving a signal (located on the linear portion of the analytical curve) two times that of the background noise; the background signal was suppressed by means of the bias adjustment of the nanoammeter read-out or subtracted from the total signal value when the Fluorispec spectrophotofluorimeter was used. In Table IV, limits of detection obtained for the fluorescent and phosphorescent vitamins are given. These values are between 0·0001 and 8 μg/ml, depending to the structure of the vitamin. Practical "sensitivity" has been determined by fluorimetry for some compounds of biological interest,[10] but these values cannot be compared with our values because of the arbitrary definition of "sensitivity". For the vitamins which fluoresce and phosphoresce, the limits of detection are about the same for fluorimetry and phosphorimetry; however for *p*-aminobenzoic acid, the limit of detection in

TABLE I.—FLUORESCENCE AND PHOSPHORESCENCE SPECTRAL CHARACTERISTICS OF SEVERAL VITAMINS

Vitamin	Fluorescence maxima*, *nm*		Phosphorescence maxima*, *nm*		Parent compound structure	Emission maxima, *nm*		Ref.*** for parent
	Excitation	Emission	Excitation	Emission		Fluorescence	Phosphorescence	
p-Aminobenzoic acid	290†	350	305	425		345	374**	(9)
Calciferol	348	420	—	NP¶		425–430††	—	(12)
Folic acid	365, 317‖	440	300, 367‖	505, 425‖		450††	NR§§	(1)
Niacinamide	—	NF¶	270	410		—	NP¶	(11)
Pyridoxine hydrochloride	290	355‡	291	425		~340‖‖	NR§§	(1)
Riboflavine§	455, 370,‖ 270‖	520	—	—		NR§§	—	—
α-Tocopherol	295	340	296	430		296¶¶	350**	(13) (9)
Vitamin A acetate	360	508	—	NP¶		510**	—	(14)

See next page for footnotes to table.

* Relative error in wavelengths = ±5 nm. Our measurements in ethanol except for riboflavin.
† A shift of λ_{ex} for fluorescence occurs for increasing concentrations (λ_{ex} shifts to 325 nm).
‡ A shift of λ_{em} for fluorescence occurs for increasing concentrations (λ_{em} shifts to 330 nm).
§ In aqueous solution, due to photolysis in ethanol.[8] Phosphorescence measurements at 77K could not be made.
‖ Secondary peak.
¶ NF or NP means that a compound does not fluoresce or phosphoresce, respectively.
** In EPA (ethanol-isopentane-diethylether 2:5:5) solvent at 77K.
†† In heptane solvent.
‡‡ In buffer solution (pH 6–8).
§§ NR means not recorded in literature.
‖‖ In acidic solution ($H_0 \sim -4$).
¶¶ In methanol.
*** Ref. is reference for emission spectra peaks.

TABLE II.—STRUCTURAL CHARACTERISTICS OF THE VITAMINS AND THE EXISTENCE OF FLUORESCENCE AND PHOSPHORESCENCE

Vitamin	Conjugated C=C system		Electron-donating heteroatom (group) adjacent to C=C	Carbonyl group	Hetero-cycle	Fluorescence		Phosphorescence	
	Aromatic	Non-aromatic				Predicted	Observed	Predicted	Observed
p-Aminobenzoic acid	+		+ (NH_2)			+	+	+	+
Ascorbic acid			+ (OH)	+		—	—	+	—
Biotin				+		—	—	+	—
Calciferol		+				+	+	—	—
Choline chloride						—	—	—	—
Folic acid			+ (NH_2, OH)	+	+	+	+	+	+
Inositol						—	—	—	—
Niacinamide				+	+	+	—	+	+
Calcium pantothenate				+		—	—	+	—
Pyridoxin hydrochloride			+ (OH)		+	+	+	+	+
Riboflavin	+			+	+	+	+	+	?*
Thiamine hydrochloride			+ (NH_2)		+	+	—	+	—
α-Tocopherol	+		+ (OH)			+	+	+	+
Vitamin A acetate		+		+		+	+	+	—

* Phosphorescence of this compound not measured (only aqueous solution studied).

TABLE III.—ABSORPTION MAXIMA, DISSOCIATION ENERGIES OF LEAST STABLE BOND AND FLUORESCENCE OF VITAMINS

			Least stable bond		Fluorescence	
Vitamin	Absorption maximum,† *nm*	Absorption maximum* *kJ/mole*	Type	Dissociation energy,‡ *kJ*/mole	Predicted	Observed
p-Aminobenzoic acid	~290	~410	C—NH$_2$	318–380	NPF‖	+
Ascorbic acid	247	485	C—OH	359–397	—	—
Biotin	234	510	C—S	213–305	—	—
Calciferol	293	406	C—C	334–418	+	+
Choline chloride	NR§	NR	C—OH	359–397	NPF	—
Folic acid	365	326	C—NH	364	+	+
Inositol	NR	NR	C—OH	359–397	NPF	—
Niacinamide	260	460	C—NH$_2$	318–380	—	—
Calcium pantothenate	NR	NR	C—NH	364	NPF	—
Pyridoxine hydrochloride	291	410	C—OH	359–397	+	+
Riboflavin	446	268	C—NH	364	+	+
Thiamine hydrochloride	267	448	C—OH	359–397	—	—
α-Tocopherol	297	402	C—O	359–397	+	+
Vitamin A acetate	328	364	C—O	359–397	+	+

* In ethanol, water, or buffer solution.

† Taken from *Organic Electronic Spectral Data*, I–IV, O. H. Wheeler and L. A. Kaplan, editors, Interscience, New York, 1946–1959.

‡ Taken from T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworths, London, 1958, and from V. I. Vedeneyen, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionization Potentials, and Electron Affinities*, Arnold, London, 1966.

§ NR means not recorded in literature.

‖ NPF means no prediction possible of fluorescence, by reason of lack of imprecision of literature data.

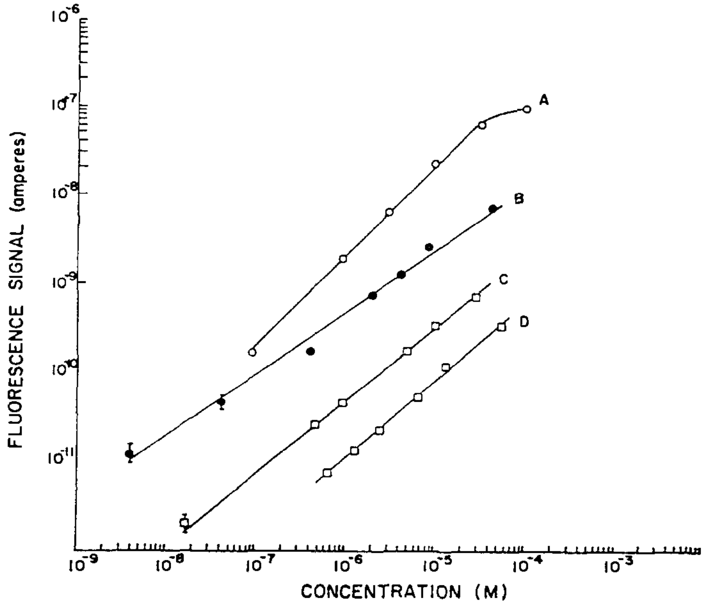


FIG. 2.—Several typical fluorimetric analytical curves:
(a) *p*-Aminobenzoic acid
(b) Pyridoxine hydrochloride
(c) Folic acid
(d) α-Tocopherol.

TABLE IV.—FLUORESCENCE AND PHOSPHORESCENCE ANALYTICAL CHARACTERISTICS OF SEVERAL VITAMINS

Vitamin	Fluorescence					Phosphorescence				
	Concentration range (*μg/ml*) of near linearity*	Slope of linear portion	Linear correlation coefficient	Std. dev.†	Limit of detection *μg/ml*	Concentration range (*μg/ml*) of near linearity*	Slope of linear portion	Linear correlation coefficient	Std. dev.†	Limit of detection *μg/ml*
p-Aminobenzoic acid	10^3	1·05	0·999	0·035	0·01	10^4	1·00	0·999	0·054	0·001
Calciferol	10^2	0·71‡	0·993	0·080	8·0	NAU§	—	—	—	—
Folic acid	10^3	0·86	0·999	0·026	0·007	$4 . 10^2$	0·81	0·995	0·085	0·004
Niacinamide	NAU§	—	—	—	—	10^2	0·95	0·995	0·059	0·2
Pyridoxine hydrochloride	10^4	0·70	0·994	0·114	0·0008	10^4	0·95	0·995	0·129	0·0008
Riboflavine‖	$5 . 10^4$	0·92	0·998	0·117	0·0001	—¶	—	—	—	—
α-Tocopherol	$2 . 10^2$	0·91	0·999	0·027	0·10	$4 . 10^2$	0·93	0·994	0·083	0·05
Vitamin A acetate	10^3	0·92	0·999	0·037	0·001	NAU§	—	—	—	—

* Near linearity means region over which slope of analytical curve is within 1 % of the values designated in the column entitled "slope of linear portion".

† Standard deviation of experimental measurements from the linear portion of the analytical curve.

‡ Value for the linear portion above the limit of detection.

§ NAU means no analytical use.

‖ In aqueous solution. All others in ethanol.

¶ No measurements possible because of aqueous solvent.

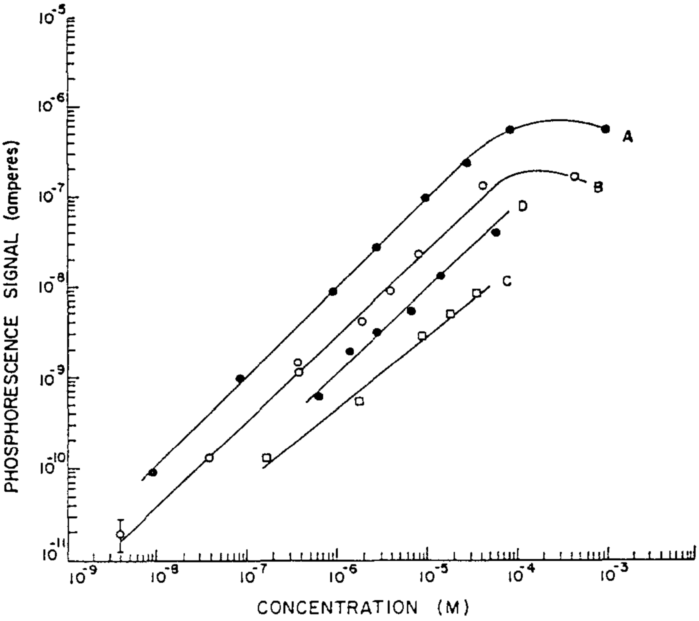


FIG. 3.—Several typical phosphorimetric analytical curves:
(a) *p*-Aminobenzoic acid
(b) Pyridoxine hydrochloride
(c) Folic acid
(d) α-Tocopherol.

phosphorimetry is lower by a factor of about 10 (see Table IV). The slopes of all analytical curves are very similar for fluorimetry and phosphorimetry and are close to unity (see Figs. 2 and 3) as expected.

In the past, fluorimetry was used for the analysis of vitamins,[1] but not phosphorimetry. However, our results show that the precision, linearity of the analytical curves, and limits of detection obtained by fluorimetry and phosphorimetry are very similar Therefore, it should be possible to use either fluorimetry or phosphorimetry for the routine determination of the nine vitamins in Table I. The choice of method will be primarily determined by the structural criteria discussed above.

Zusammenfassung—Die Fluoreszenz- und Phosphoreszenzeigenschaften von 14 Vitaminen wurden ermittelt. Auftreten oder Abwesenheit von Fluoreszenz und Phosphoreszenz wurden mit Voraussagen verglichen, die an Hand der Molekülstruktur getroffen wurden. Analytisch brauchbare Fluoreszenzen wurden gefunden bei p-Aminobenzoesäure, Folsäure, Calciferol, Pyridoxin-Hydrochlorid, Lactoflavin, α-Tocopherol und Vitamin A, analytisch brauchbare Phosphoreszenzen bei *p*-Aminobenzoesäure, Folsäure, Nicotinsäureamid, Pyridoxin-Hydrochlorid und α-Tocopherol. Alle anderen Vitamine fluoreszierten und phosphoreszierten nicht oder konnten wegen experimenteller Schwierigkeiten nicht gemessen werden. Die komplementäre Natur von Fluorimetrie und Phosphorimetrie kommt in diesen Untersuchgen zum Ausdruck.

Résumé—On a évalué les caractéristiques de fluorescence et de phosphorescence de 14 vitamines. On a comparé l'existence ou l'absence de fluorescence et de phosphorescence aux prévisions basées sur la

structure moléculaire. Des signaux de fluorescence analytiquement utiles ont été obtenus pour l'acide *p*-aminobenzoïque, l'acide folique, le calciférol, le chlorhydrate de pyridoxine, la riboflavine, l'α-tocophérol et la vitamine A, tandis que des signaux de phosphorescence analytiquement utiles ont été obtenus pour l'acide *p*-aminobenzoïque, l'acide folique, le niacinamide, le chlorhydrate de pyridoxine et l'α-tocophérol. Toutes les autres vitamines n'émettent pas de flourescence ou de phosphorescence, ou ne peuvent être mesurées à cause de difficultés expérimentales. La nature complémentaire de la fluorimétrie et de la phosphorimétrie est évidente dans ces études.

REFERENCES

1. S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, Vol. I, p. 230. Academic Press, New York, 1966, Vol. II, p. 291. Academic Press, New York, 1969.
2. M. Zander, *The Applications of Phosphorescence to the Analysis of Organic Compounds*, Academic Press, New York, 1968.
3. J. D. Winefordner, W. J. McCarthy and P. A. St. John, *Methods of Biochemical Analysis*, D. Glick, Ed., Vol. 15, Interscience, New York, 1967.
4. J. D. Winefordner, P. A. St. John and W. J. McCarthy, *Fluorescence Assay in Biology and Medicine*, Vol. II, p. 42. Academic Press, New York, 1969.
5. R. Zweidinger and J. D. Winefordner, *Anal. Chem.*, 1970, **42**, 639.
6. T. C. O'Haver and J. D. Winefordner, *J. Chem. Educ.*, 1969, **46**, 241.
7. J. D. Winefordner and M. Tin, *Anal. Chim. Acta*, 1964, **31**, 239.
8. J. Koziol and E. Knobloch, *Biochim. Biophys. Acta*, 1965, **102**, 289.
9. E. J. Bowen, *Luminescence in Chemistry*, Van Nostrand, London, 1968.
10. D. E. Duggan, R. L. Bowman, B. B. Brodie and S. Udenfriend, *Arch. Biochem. Biophys.*, 1957, **68**, 1.
11. R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley, New York, 1969.
12. A. N. Nikitin, M. D. Galin, G. S. Ter-Sarkisian and B. M. Mikhailov, *Opt. Spectry*, 1959, **6**, 226.
13. I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965.
14. D. Balke and R. S. Becker, *J. Am. Chem. Soc.*, 1967, **89**, 5061.

Talanta, 1972, Vol. 19, pp. 31 to 36. Pergamon Press. Printed in Northern Ireland

MICRODETERMINATION OF α-AMINO ACIDS BY SPECTROPHOTOMETRIC AND TITRIMETRIC METHODS

W. I. AWAD
Department of Chemistry, University College for Women, Ain Shams University, Cairo
U.A.R.

S. NASHED, S. S. M. HASSAN and R. F. ZAKHARY
Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, U.A.R.

(*Received* 16 *April* 1971. *Accepted* 22 *June* 1971)

Summary—Micro-methods for spectrophotometric and oxidimetric determination of α-amino-acids are described. They are based on a reaction of the acids with *peri*-naphthindan-2,3,4-trione hydrate at pH 2.5 to give a red precipitate of dihydroxy-*peri*-naphthindenone. The red product is dissolved and measured either spectrophotometrically at 243 nm or titrimetrically by reaction with iodine or *N*-bromosuccinimide. The results obtained by the three methods are concordant, the average recovery being 98%.

MANY METHODS have been reported for the determination of α-amino-acids. Alkalimetric,[1] acidimetric,[2] manometric,[3] gasometric,[4] and chromatographic[5] measurements of nitrous oxide, nitrogen, ammonia, carbon dioxide and aldehydes produced by reactions with suitable reagents have been proposed. Direct alkalimetric[6] and complexometric[7] determination of the free acid after treatment with excess of formaldehyde and copper salts are employed. Enzymatic,[8] mass spectrometric[9] and conductometric[10] methods have been also utilized.

However, few colorimetric and redox reactions are known for amino-acid determination. Colorimetric reactions with ninhydrin,[11] 3,5-dibromosalicyldehyde[12] and *o*-diacetylbenzene[13] have been mentioned. A method based on a reaction of *N*-ethylmaleimide with carboxydithiocarbamate, formed by the action of carbon disulphide on the acid, is described.[14] An oxidimetric method based on deamination of the acid followed by oxidation of the resulting hydroxy-acid with vanadium(V) has been used.[15]

Peri-naphthindan-2,3,4-trione hydrate has been proposed for the determination of α-amino-acids by measuring the amount of carbon dioxide,[16] ammonia,[17] and aldehydes[18] produced. In the present work this reagent is used in the development of new colorimetric and redox methods for amino-acid determination.

EXPERIMENTAL

Reagents

All reagents were of analytical grade unless otherwise specified.

Peri-*naphthindan-2,3,4-trione hydrate* was prepared as described previously.[18,19]

*Dihydroxy-*peri*-naphthindenone* was prepared by reduction of the trione with ascorbic acid.[20]

Citrate buffer solution. Sodium citrate trihydrate (2·06 g) and 19·16 g of citric acid monohydrate were dissolved in 500 ml of water.

The α-amino-acids used were of purity not less than 99%.

Procedure

Spectrophotometric determination of α-amino-acids. Construct a standard calibration curve as follows. Dissolve 1·765 mg of dihydroxy-*peri*-naphthindenone in 50 ml of methanol. Then take 1·5, 2, 2·5, 3, 3·5, 4, 4·5 and 5 ml of this solution in 10-ml measuring flasks and make up to the mark with methanol. Measure the absorbance of these solutions at 342 nm in 10-mm cuvettes within 15 min, using methanol in the reference cell. Draw a graph of the absorbance against the concentration of amino-acid nitrogen (1 μg of dihydroxy-*peri*-naphthindenone ≡ 0·066 μg of amino-acid nitrogen).

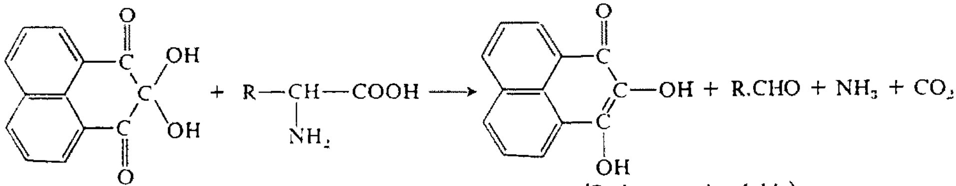
Into a 25-ml round bottom flask, introduce 4 ml of 0·1% *peri*-naphthindan-2,3,4-trione hydrate solution in distilled water and 1 ml of the citrate buffer solution. Add 0·4 ml of 8m*M* α-amino-acid solution in water (equivalent to 44·8 μg of amino-acid nitrogen). Heat the flask under reflux for 1 hr at 100°, cool in ice and filter (Whatman No. 42 paper). Wash several times with cold water. Dissolve the red precipitate of dihydroxy-*peri*-naphthindenone in methanol into a 50-ml graduated flask. Measure the absorbance at 342 nm in a 10-mm cell against a blank.

Titrimetric determination of α-amino-acids with iodine. Dissolve the dihydroxy-*peri*-naphthindenone precipitate in 25 ml of methanol in a 250-ml conical flask. Add 100 ml of water and 5 ml of 0·004*N* iodine. After 5 min titrate the excess of iodine with 0·004*N* sodium thiosulphate, using starch as indicator (1 ml of 0·004*N* iodine ≡ 21 μg of amino-acid nitrogen).

Titrimetric determination of α-amino-acid with N-*bromosuccinimide.* Dissolve the red precipitate in 50 ml of 1:1 acetic acid–water in a 250-ml conical flask. Dilute with water to 150 ml, add 5 ml of 4% potassium iodide solution and 1 ml of 1% starch solution and titrate with 0·004*N* *N*-bromosuccinimide (1 ml of 0·004*N* *N*-bromosuccinimide ≡ 21 μg of amino-acid nitrogen).

RESULTS AND DISCUSSION

Peri-naphthindan-2,3,4-trione hydrate (I) decomposes α-amino-acids quantitatively with the formation of the corresponding aldehyde having one carbon atom less, ammonia, carbon dioxide and dihydroxy-*peri*-naphthindenone (II) according to the equation:



(Colourless, water-soluble) (I)

(Red, water-insoluble) (II)

Since one molecule of dihydroxy-*peri*-naphthindenone is produced for each molecule of α-amino-acid, this reaction may be used for amino-acid determination. The reaction is quantitative in a citrate buffer solution at pH 2·5 and a low blank value is obtained.

Spectrophotometric methods

Absorption spectra. The absorption spectra show maxima at 320 nm (ε 1·22 × 10^3 $\text{l.mole}^{-1}.\text{mm}^{-1}$) for the naphthindantrione and 342 nm (ε 1·14 × 10^3 $\text{l.mole}^{-1}.\text{mm}^{-1}$) for the dihydroxynaphthindenone (Fig. 1). Because of the equal absorption by both compounds over a wide wavelength range, prior separation is necessary; in that case an excess of the reagent does not adversely affect the accuracy of the method.

Beer's law is obeyed (for dihydroxy-*peri*-naphthindenone) in the concentration range equivalent to 0·1–2 μg of amino-acid nitrogen per ml and only one calibration curve is required for all α-amino-acids.

Effect of pH. Dihydroxy-*peri*-naphthindenone dissolves in methanol to give a red

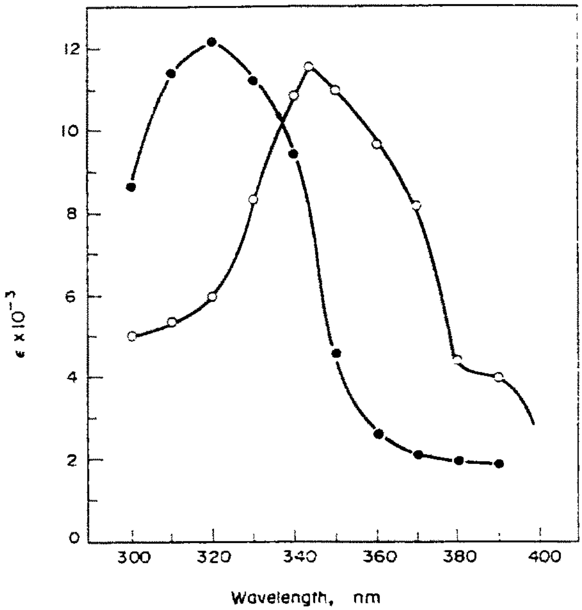


FIG. 1

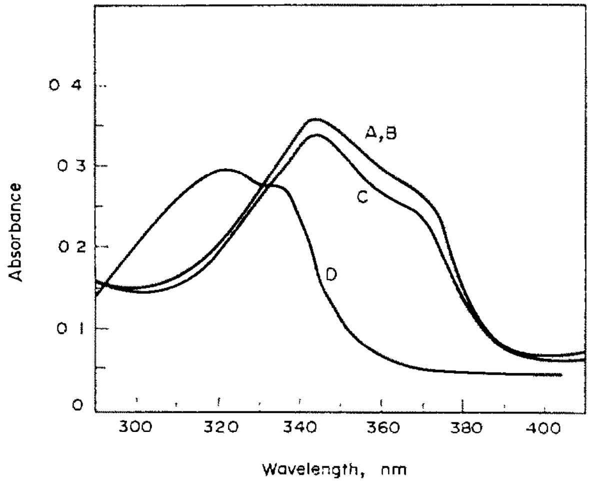


FIG. 2

solution and in glacial acetic acid to give a yellow one. Both solutions absorb at around 340 nm with equal molar absorptivity, indicating that the colour intensity at this wavelength is independent of the acidity.

Effect of standing time. The absorbance of methanolic solutions containing different concentrations (up to 12 μg/ml) of dihydroxy-*peri*-naphthindenone was measured after 1, 30 and 120 min and 24 hr. It was observed that the colour intensity

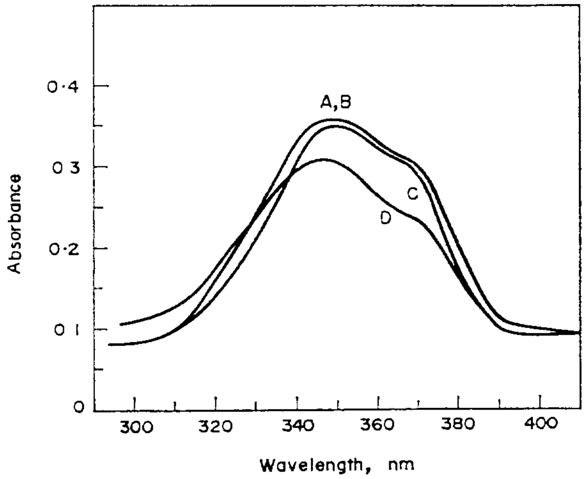


Fig. 3.

remained stable for 30 min, after which fading took place. On standing for 2 hr the intensity decreased by 5–10%. After 24 hr the dihydroxy-*peri*-naphthindenone changed (probably by air-oxidation) to *peri*-naphthindan-2,3,4-trione and the absorption maximum was shifted to 320 nm (Fig. 2). However, the dihydroxy compound was more stable in glacial acetic acid medium and 85% of the colour intensity remained after 24 hr (Fig. 3).

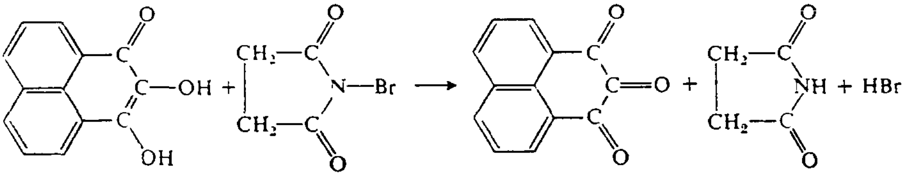
Determination of α-amino-acids. A number of α-amino-acids were analysed for amino-nitrogen content. The results (Table I) show an average recovery of 98·2% and a mean absolute error of ±0·3%. Amino-acids containing thiol groups (*e.g.*, cysteine hydrochloride) give high recoveries probably because of the interference of the thiol group in the reduction reaction.

Table I.—Microdetermination of α-amino-acids by reaction with *peri*-naphthindan-2,3,4-trione hydrate

Sample	Theory	Amino-acid nitrogen, %		
		Spectro-photometric	Titrimetric (iodine)	Titrimetric (*N*-bromosuccinimide)
Glycine	18·65	19·9	18·7	18·7
Phenylalanine	8·48	8·6	8·5	8·5
Glutamic acid monohydrate	8·48	8·4	8·4	8·4
Aspartic acid	10·52	10·2	10·1	10·2
Leucine	10·67	10·3	10·3	10·2
Methionine	9·38	9·2	9·2	9·2
Threonine	11·75	11·3	11·5	11·4
Serine	13·32	12·8	12·7	12·8

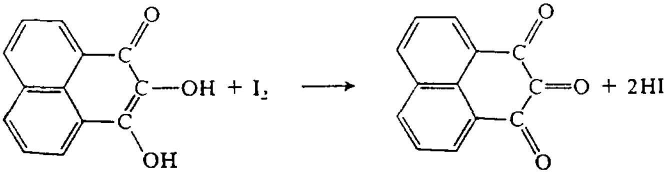
Titrimetric methods

Reaction with N-*bromosuccinimide. N*-Bromosuccinimide quantitatively oxidizes the ene-diol group in dihydroxy-*peri*-naphthindenone to give *peri*-naphthindan-2,3,4-trione. The reaction proceeds according to the equation:



For determining α-amino-acids, the equivalent amount of the dihydroxy compound is separated from the reaction medium by filtration, dissolved in acetic acid and titrated directly with standard *N*-bromosuccinimide solution.

Reaction with iodine. The ene-diol group of dihydroxy-*peri*-naphthindenone reacts with iodine quantitatively according to the equation:



Excess of iodine solution is added to the dihydroxy compound (itself equivalent to the amino-acid) and the iodine remaining after reaction is titrated with sodium thiosulphate.

Determination of α-amino-acids. Many samples of α-amino-acids were analysed by oxidimetric titration of the equivalent amount of dihydroxy-*peri*-naphthindenone obtained in the reaction with the trione. With *N*-bromosuccinimide, the results obtained show an average recovery of 97·8% and a mean absolute error of ±0·3%. With iodine, the mean absolute error is ±0·3%, the average recovery being 98·4% (Table 1).

Zusammenfassung—Mikromethoden zur spektrophotometrischen und oxidimetrischen Bestimmung von α-Aminosäuren werden beschrieben. Sie beruhen auf der Reaktion der Säuren mit *peri*-Naphthindan-2,3,4-trion-Hydrat bei pH 2·5; es entsteht ein roter Niederschlag von Dihydroxy-*peri*-naphthindenon. Das rote Produkt wird gelöst und entweder spektrophotometrisch bei 243 nm oder titrimetrisch durch Reaktion mit Jod oder *N*-Bromsuccinimid bestimmt. Die Ergebnisse der drei Methoden stimmen überein, im Durchschnitt beträgt die Ausbeute 98%.

Résumé—On décrit des microméthodes pour la détermination spectrophotométrique et oxydimétrique des α-amino acides. Elles sont basées sur une réaction des acides avec l'hydrate de *peri*-naphtindan-2,3,4-trione à pH 2,5, donnant un précipité rouge de dihydroxy-*peri*-naphtindéone. Le produit rouge est dissous et mesuré, soit spectrophotométriquement à 243 nm, soit titrimétriquement par réaction avec l'iode ou le N-bromosuccinimde. Les résultats obtenus par les trois méthodes sont concordants, la récupération moyenne étant de 98%.

REFERENCES

1. D. van Slyke, D. MacFadyer and P. Hamilton, *J. Biol. Chem.*, 1941, **141**, 671.
2. A. Patchornik and Y. Shalitin, *Anal. Chem.*, 1961, **33**, 1887.
3. D. van Slyke, R. Dillon, D. MacFadyer and P. Hamilton, *J. Biol. Chem.*, 1941, **141**, 627.
4. M. Renard and P. Deschamps, *Mikrochim. Acta*, 1951, **37**, 665.
5. M. Bier and P. Teitelbaum, *Ann. N.Y. Acad. Sci.*, 1959, **72**, 641.
6. W. Taylor, *Analyst*, 1957, **82**, 488.
7. B. Gauthier and M. Maréchal, *Ann. Pharm. Franc.* 1962, **20**, 156.
8. H. Malmstadt and T. Hadjiioannou, *Anal. Chem.* 1963, **35**, 14.
9. G. Junk and H. Svec, *Anal. Chim. Acta*, 1963, **28**, 164.
10. M. Trnková and M. Voldan, *Cesk. Farm.*, 1963, **12**, 182.
11. S. Moore and W. Stein, *J. Biol. Chem.*, 1954, **211**, 907.
12. K. Yuhi, *J. Pharm. Soc. (Japan)*, 1961, **81**, 297.
13. R. Riemschneider and J. Wierer, *Z. Anal. Chem.*, 1963, **193**, 186.
14. Z. Peizker, *Collection Czech. Chem. Commun.*, 1960, **25**, 1514.
15. S. Rao, H. Rathi and J. Gau, *Anal. Chim. Acta*, 1961, **25**, 136.
16. R. Moubasher and A. Sina, *J. Biol. Chem.*, 1949, **180**, 681.
17. R. Moubasher, W. I. Awad and A. Othman, *ibid.*, 1950, **184**, 693.
18. R. Moubasher and W. I. Awad, *ibid.*, 1949, **179**, 915.
19. G. Errera, *Gazz. Chim. Ital.*, 1913, **43**, 593; 1914, **44**, 18.
20. R. Moubasher, *J. Biol. Chem.*, 1948, **176**, 529.

Talanta, 1972, Vol. 19, pp. 37 to 43. Pergamon Press. Printed in Northern Ireland

INDIRECT NEAR-INFRARED SPECTROPHOTOMETRIC DETERMINATION OF SILICATE BY THE 2-AMINO-4-CHLOROBENZENETHIOL METHOD

LOUIS A. TRUDELL* and D. F. BOLTZ
Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

(*Received* 1 *March* 1971. *Accepted* 3 *August* 1971)

Summary—An indirect near-infrared spectrophotometric method for the determination of silicate, based on the absorbance of an equivalent amount of molybdenum-2-amino-4-chlorobenzenethiol complex in chloroform solution, has been developed. The green chloroform solution has an absorbance maximum at 715 nm. The development of the spectrophotometric method for the determination of silicate included a study of a buffer system for the purpose of maintaining the pH within a narrow optimum pH range, complex stability, effect of diverse ions, and conformity to Beer's law. The limit of detection is 0·034 μg of silicon per ml of aqueous heteropoly acid solution.

THE MAJORITY of the spectrophotometric methods for the determination of silicate that have been reported in the literature are based on the heteropoly acid chemistry of silicate. The very sensitive indirect methods involve the partitioning of molybdosilic acid from excess of molybdate by extraction with organic solvents followed by the decomposition of the extracted heteropoly acid and subsequent measurement of the molybdate in the decomposition products. The molybdate, which is equivalent to the amount of silicon present in the original sample, can be measured without further treatment by spectrophotometry[1,2] and by atomic-absorption spectrometry.[2,3] Other methods have been reported in which the molybdate is reacted with thiocyanate,[4] ammonium 1-pyrrolidinecarbodithioate,[5] or hydrogen peroxide[6] and the resulting molybdenum products are measured spectrophotometrically.

The method proposed in this paper differs from all previous spectrophotometric heteropoly acid methods for silicate because it is an indirect near-infrared method. The method is based on the measurement of the absorptivity of the chloroform extract of a green complex that molybdenum forms with 2-amino-4-chlorobenzenethiol hydrochloride.[7] The absorptivity of the molybdenum-2-amino-4-chlorobenzenethiol complex, in chloroform, has been utilized successfully for the indirect determination of phosphorus.[8]

The procedure developed by Kirkbright and Yoe for the formation and extraction of the molybdenum complex and later used for the indirect determination of phosphorus has been improved as a result of the studies associated with the method reported in this paper.

EXPERIMENTAL

Reagents

Standard silicate solution. Dissolve 5·50 g of sodium metasilicate, $Na_2SiO_3{\cdot}9H_2O$, in water and dilute to 1 litre. The pH of this solution is about 11·5. Standardize this solution gravimetrically and use a microburette to transfer sufficient silicate solution to a 1-litre volumetric flask so that on dilution to the mark, the final silicate solution contains 2·0 μg of silicon per ml.

---

* Present address: Division of Mathematics and Science, Macomb County Community College, Warren, Michigan 48093, U.S.A.

Ammonium molybdate solution. Dissolve 25·0 g of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in water and dilute to 500 ml.

Dilute ammonia solution. Prepare a 0·25*M* ammonia solution by diluting 17·5 ml of concentrated ammonia solution to 1 litre with water.

Sulphate–bisulphate buffer solution. Dissolve 106·4 g of anhydrous sodium sulphate and 20·68 g of sodium bisulphate, $NaHSO_4\cdot H_2O$, in water and dilute to 1 litre.

2-Amino-4-chlorobenzenethiol hydrochloride solution. Dissolve 0·25 g of 2-amino-4-chlorobenzenethiol hydrochloride in 5·0 ml of 95% ethanol. Prepare the reagent solution fresh every two days.

Extractant mixture. Mix 1 volume of 1-pentanol with 5 volumes of diethyl ether. Prepare the mixture fresh each day.

All aqueous solutions were prepared with reagent grade chemicals and redistilled water. The solutions were stored in paraffin-lined bottles to avoid silica contamination. Reagent-grade organic solvents were used for the extractions that are specified in the procedure.

Procedure

Transfer to a 125-ml separatory funnel a sample containing 2–8 μg of silicon in the form of soluble silicate. Add 1·0 ml of hydrochloric acid (1 + 1) and dilute the acidified sample solution to 45 ml with redistilled water. Add 5·0 ml of the ammonium molybdate solution, mix, and allow the solution to stand for 20 min to ensure complete formation of the silicomolybdic acid. The pH of this solution should be about 1·4.

Add 30 ml of hydrochloric acid (1 + 1) and 20 ml of 5:1 ethyl ether–1-pentanol extractant mixture. Shake the separatory funnel vigorously on a mechanical shaker for 1 min. Rinse the stopper with 1–2 ml of fresh extractant mixture and collect the rinsings in the separatory funnel. Allow the layers to separate for 3 min, then withdraw the lower aqueous layer and discard it. Wash the organic phase twice, each time with 25 ml of hydrochloric acid.(1 + 10). Each washing consists of shaking the organic phase with the wash solution for 15 sec, allowing the two phases to separate, and withdrawing and discarding the lower aqueous phase. After the second wash is completed, rinse the funnel tip with distilled water.

Add 20 ml of 0·25*M* ammonia to the funnel and shake vigorously for 30 sec. After the layers have separated, carefully transfer the lower aqueous solution containing the decomposition products of silicomolybdic acid to a 100-ml volumetric flask. Rinse the funnel and funnel stopper several times with a total of 20–30 ml of distilled water and add the rinsings to the volumetric flask. Acidify the flask contents with 4·0 ml of hydrochloric acid solution (1 + 10). Add 25 ml of the sulphate–bisulphate buffer solution, dilute to the mark with distilled water, and mix well. The pH of this solution should be between 1·9 and 2·3.

Transfer a 25·00-ml aliquot of the buffered molybdate solution to a clean 125-ml separatory funnel that has a cotton plug inserted into its tip. Numerous samples may be simultaneously treated up to this point of the procedure and the aliquots of the buffered molybdate solutions may be allowed to stand in their respective separatory funnels until they are used to complete the procedure that follows.

Add 0·25 ml of the ethanolic reagent solution, swirl the funnel to mix its contents, and allow the solution to stand for 15–60 min. Add 10·00 ml of chloroform, start a mechanical timer, and shake the funnel vigorously on a mechanical shaker for 1 min. Allow the phases to separate for a few sec, then rinse a 10-mm silica cell with small portions of the chloroform extract that have been drained through the cotton plug. Finally, fill the cell with the green chloroform extract and exactly 3 min after the chloroform extraction step was begun, place the cell in the spectrophotometer and quickly measure the absorbance of the extract at 715 nm with chloroform in the reference cell. Correct for the absorbance of a reagent blank extract. Refer the corrected absorbance to a standard calibration graph

So that the analyst may use his time more efficiently, the following sequence of steps is recommended for the completion of the determination of a series of sample solutions: (1) add the ethanolic reagent solution to three of the separatory funnels containing 25·00-ml aliquots of the buffered molybdate solution; (2) after 15 min, add the ethanolic reagent solution to three other aliquots of the buffered molybdate solutions; (3) complete the extraction and measurement of each of the three solutions prepared in step (1) (these operations will require a total of 12–15 min); (4) add the ethanolic reagent solution to three more aliquots of buffered molybdate solutions; (5) complete the extraction and measurement of each of the three solutions prepared in step (2). Continue the sequence of steps until all molybdate aliquots have been taken completely through the recommended procedure.

RESULTS AND DISCUSSION

Absorption spectra

Figure 1 shows the near-infrared absorption spectra for the chloroform extracts of the molybdenum-2-amino-4-chlorobenzenethiol complex. The amount of the complex in chloroform solution is equivalent to a specific amount of silicon in the original

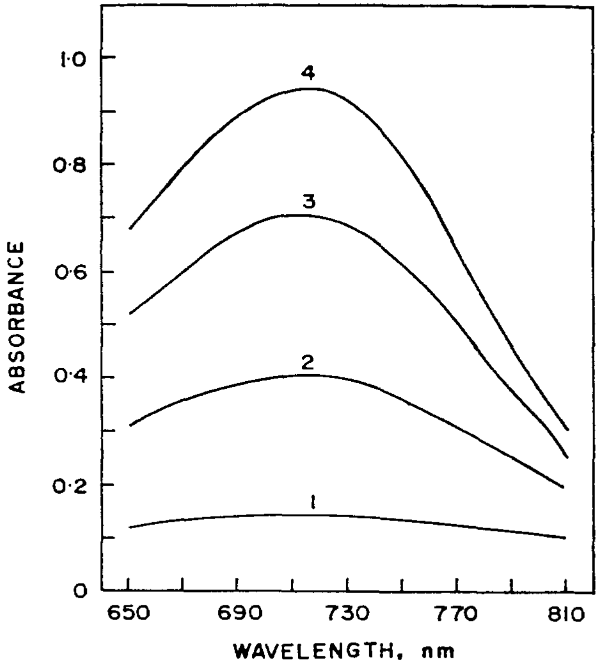


FIG. 1. Characteristic near-infrared spectra of molybdenum-2-amino-4-chlorobenzenethiol in chloroform *vs.* chloroform.
(1) Reagent blank equivalent in chloroform,
(2) 0·10 ppm of silicon equivalent in chloroform,
(3) 0·20 ppm of silicon equivalent in chloroform,
(4) 0·30 ppm of silicon equivalent in chloroform.

sample. The chloroform extract of the reagent blank exhibits significant absorbance and must be subtracted from the absorbances obtained for the silicate samples. The organic reagent used to form the molybdenum complex does not absorb in the spectral region 500–1000 nm.

Effects of solution variables

Silicon concentration. Conformity to Beer's law was observed for the molybdenum equivalent to 0·05–0·20 μg of silicon per ml of chloroform solution, *i.e.*, 2–8 μg of silicon in the original 50 ml of silocomolybdic acid solution. The optimum concentration range is equivalent to 0·075–0·175 μg of silicon per ml of chloroform, *i.e.* 3–7 μg of silicon in the original 50 ml of molybdosilicic acid solution.

The various silicon concentrations that have been or will be mentioned in this paper should be clarified and delineated. The basis of possible confusion lies in the fact that there are four solutions of importance, *viz.*, (1) the original 50 ml of aqueous silicomolybdic acid solution, (2) the 100 ml of buffered molybdate solution, (3) the 25·00 ml aliquot of the buffered molybdate solution that is taken for the molybdenum determination according to the recommended procedure, and (4) the 10·00 ml chloroform solution of the molybdenum complex formed from 25% of the total molybdenum recovered from the silicomolybdic acid. Table I indicates the equivalent silicon concentration in each of these solutions when a sample containing 4·0 μg of silicon is taken for analysis.

TABLE I.—EQUIVALENT SILICON CONCENTRATION IN VARIOUS PREPARED SOLUTIONS

Solution	Total amount of Si, μg	Equiv. Si concn., μg/ml
Original 50-ml silicomolybdic acid solution	4·0	0·080
100-ml buffered molybdate solution	4·0	0·040
25·00-ml aliquot of buffered molybdate solution	1·0	0·040
10·00-ml chloroform extract from 25% of recovered molybdate	1·0*	0·10†

* Theoretical amount of silicon extracted by chloroform.

† Theoretical concentration of silicon extracted by chloroform.

Conditions for the formation and extraction of molybdosilic acid. The effects of acidity and molybdate concentration on the formation of silicomolybdic acid,[1,2,9] the effect of the acidity on the extent of extraction[1,2] and the choice of the solvent system used for the extraction[1] have been previously investigated. The optimum conditions for the most efficient formation and extraction of the heteropoly acid were chosen for this study.

pH of the molybdate solution. Previous studies have shown that the optimum pH range for formation of the molybdenum-2-amino-4-chlorobenzenethiol complex is 1·9–3·3 whereas the optimum pH range for chloroform extraction of the complex is 1–2·3,[7] The procedure that has been used for the pH adjustment of the molybdate solution[7,8] was found to be quite unsatisfactory because of the amount of time required to complete the acidity adjustment. The difficulty that was encountered was to keep within the narrow optimum pH range and this was probably due to the fact that only 3·0 ml of a Clark and Lubs' buffer solution (0·006*M* in HCl and 0·05*M* in KCl) was used and it provided little, if any, buffer capacity. The tedium and inconvenience associated with having to carefully monitor the pH adjustment of the molybdate solutions with a pH-meter indicated the need for a more suitable means of adjusting and maintaining the pH of the solution. The sulphate–bisulphate buffer system, studied by Jeffreys and Swift,[10] was adapted for use in the acidity adjustment because other anions and organic reagents that are commonly used in buffer solutions for the pH 2 region are known to interfere with this method of molybdenum determination.

Several studies were made concerning the acidification step. One study showed that the final 100-ml molybdate solution had a pH of about 2·1 when 20·0 ml of the dilute ammonia solution were used to strip the molybdate from silicomolybdic acid and when the ammoniacal solution was treated with 4·0 ml and 25·0 ml of hydrochloric acid (1 + 10) and sulphate–bisulphate buffer solution, respectively. Another study showed that these volumes can be significantly varied with little effect on the resulting pH of the final solution. Table II summarizes the changes in pH observed corresponding to the indicated changes in the volumes of the individual solutions that were involved in the acidity adjustment. As a consequence of this study, it was predicted that the volumes of the dilute ammonia solution and the buffer solution could be measured accurately enough in a 25-ml graduated cylinder, and that of the hydrochloric acid solution with a measuring pipette, and the pH of the final buffered

TABLE II.—EFFECT OF CHANGE IN VOLUME OF SOLUTIONS INVOLVED IN THE ACIDITY ADJUSTMENT OF THE MOLYBDATE BACK-EXTRACT

Solution	Recommended volume, *ml*	Change in volume, *ml*	Average pH change
0·25*M* NH_3	20·0	±1·0	±0·05
HCl (1 + 10)	4·0	±0·5	±0·05
SO_4^{-2}–HSO_4^- buffer	25·0	±1·0	±0·11

molybdate solution would be within the limits necessary for optimum formation and extraction of the molybdenum complex. These predictions were tested by randomly selecting 12 molybdate solutions as they, among others, were prepared for use during a period of several days. The pH of each of these 12 solutions was measured with a pH-meter. The results of this random pH study are summarized in Table III and they demonstrate the effectiveness of the sulphate–bisulphate system for maintaining the molybdate solutions within the desired pH range of 1·9–2·3.

Extraction time for the molybdenum complex. A 1-min shaking period is sufficient for the complete extraction of the molybdenum complex.

Stability of the molybdenum complex. The green molybdenum-2-amino-4-chlorobenzenethiol complex in chloroform undergoes slow photodecomposition in room light and rapid photodecomposition when subjected to the radiation passing through the sample cell in the Cary spectrophotometer used. The rate of absorbance decrease is about 0·3% per min when the chloroform extract is allowed to stand in room light and 3·6% per min when the sample cell remains in the cell compartment of an instrument where the radiation emitted by the source passes continually through the cell. These observed rates of absorbance decrease do not agree with those reported for the determination of molybdenum with this reagent, *viz.*, a decrease of only 6% after 4 hr and 9% after 6 hr.[7] It should be mentioned that the larger rate of absorbance decrease cannot be attributed to the use of the sulphate–bisulphate buffer solution, because the instability of the complex was also observed when the molybdenum determinations were performed exactly as recommended in the original method.

It is postulated that the lower rate of absorbance decrease reported in the original method for molybdenum was because the sample was kept in relative darkness or in the cell compartment of the Beckman DK-2 spectrophotometer. The optical system of DK-2 spectrophotometer is different from that of the Cary 14 spectrophotometer when the latter is in the near-infrared mode of operation. In the former instrument, the radiation incident to the sample cell is monochromatic whereas the source radiation remains polychromatic in the Cary 14 spectrophotometer until after it has passed through the sample cell and then reaches the monochromator. Therefore, the flux reaching the sample cell and which is responsible for the photodecomposition of the green molybdenum complex is considerably less in the Beckman DK-2 spectrophotometer than in either room light or the Cary 14 spectrophotometer.

TABLE III.—SUMMARY OF pH VARIATIONS OF RANDOMLY-SELECTED BUFFERED MOLYBDATE SOLUTIONS

Number of solutions measured	12
pH range	2·07–2·11
Average pH	2·08
Average deviation	0·01

TABLE IV.—INTERFERING IONS

Ion	Added	Amount added, *μg of ion*	Relative error, %	Permissible amount*, *ppm*
Al^{3+}	$Al(ClO_4)_3$	5000	−8·0	50
Fe^{3+}	$FeNH_4(SO_4)_2$	250	−7·9	1
Pb^{2+}	$Pb(C_2H_3O_2)_2$	2500	−7·9	25
Zn^{2+}	$Zn(ClO_4)_2$	5000	−8·1	50
AsO_2^-	$NaAsO_2$	5000	+9·3	25
AsO_4^{3-}	Na_2HAsO_4	2500	+36	10
$Cr_2O_7^{2-}$	$K_2Cr_2O_7$	250	−7·9	1
F^-	KF	500	+16	5
NO_2^-	KNO_2	50	−13	0
PO_4^{3-}	KH_2PO_4	1250	+7·1	10
VO_3^-	NH_4VO_3	250	−14	1

* Causes less than 5·0 per cent relative error in determination of 4·0 μg of silicon per 50 ml of aqueous heteropoly acid solution.

Effect of diverse ions. The effect of 5000 μg of diverse ions in solutions containing 4·0 μg of silicon was investigated. The effect of larger amounts was not investigated. The following ions did not interfere with the determination of silicon: ammonium, calcium, chromium(III), cobalt(II), copper(II), magnesium, manganese(II), nickel, potassium, silver, sodium, acetate, bromide, chloride, molybdate, nitrate, oxalate, perchlorate, permanganate, sulphate and tungstate. The permissible amounts of the interfering ions are listed in Table IV. No attempt was made to avoid the interferences caused by these ions.

Precision

An estimate of the precision of the recommended procedure was obtained from the results of 6 samples, each containing 4·0 μg of silicon in the original 50 ml of aqueous silicomolybdic acid solution. The mean absorbance of the molybdenum complex in chloroform obtained from these samples was 0·698 when measured at 715 nm against chloroform. The standard deviation was 0·017 and the relative standard deviation 2·4%. The limit of detection was ascertained from a series of six determinations of reagent blank solutions. A mean absorbance value of 0·145 and a standard deviation of 0·024 were obtained. The limit of detection, when based on the equations cited by Kaiser,[11] is equivalent to about 0·043 μg of silicon per ml of chloroform or about 1·7 μg of silicon in the original 50-ml aqueous silicomolybdic acid solution (0·034 ppm of silicon).

Sensitivity

The effective molar absorptivity, based on the original 50 ml of aqueous silicomolybdic acid solution, is $1{\cdot}97 \times 10^4$ $l.mole^{-1}.mm^{-1}$ at 715 nm. The molar absorptivity is $1{\cdot}58 \times 10^4$ $l.mole^{-1}.mm^{-1}$ when based on the equivalent concentration of silicon in the chloroform extract.

Zusammenfassung—Zur Bestimmung von Silikat wurde eine indirekte spektrophotometrische Methode im nahen Infrarot entwickelt. Sie beruht auf der Messung der Extinktion einer äquivalenten Menge des Komplexes aus Molybdän und 2-Amino-4-chlorthiophenol in Chloroformlösung. Die grüne Chloroformlösung hat ein Absorptionsmaximum bie 715 nm. Bei der Entwicklung des spektrophotometrischen Verfahrens zur Silikatbestimmung wurde auch ein Puffersystem untersucht, das den pH in einem engen optimalen Bereich konstant hält, sowie die Stabilität des Komplexes, der Einfluß verschiedener Ionen und die Gültigkeit des Beerschen Gesetzes. Die Nachweisgrenze beträgt 0,034 μg Silicium pro ml wäßriger Heteropolysäurelösung.

Résumé—On a élaboré une méthode spectrophotométrique indirecte dans le proche infra-rouge pour le dosage du silicate, basée sur l'absorption d'une quantité équivalente du complexe molybdene-2-amino 4-chlorothiophénol en solution chloroformique. La solution chloroformique verte a un maximum d'absorption à 715 nm. Le développement de la méthode spectrophotométrique pour le dosage du silicate comprend une étude d'un systéme tampon dans le but de maintenir le pH dans un domaine optimal étroit de pH, de la stabilité du système, de l'influence de divers ions et de la conformité à la loi de Beer. La limite de détection est de 0,034 μg de silicium par ml de solution aqueuse d'hétéropolyacide.

REFERENCES

1. L. A. Trudell and D. F. Boltz, *Anal. Chem.*, 1963, **35**, 2122.
2. T. R. Hurford and D. F. Boltz, *ibid.*, 1968, **40**, 379.
3. G. F. Kirkbright, A. M. Smith, and T. S. West, *Analyst*, 1967, **92**, 411.
4. F. Umland and G. Wünsch, *Z. Anal. Chem.*, 1965, **213**, 186.
5. M. B. Kalt and D. F. Boltz, *Anal. Chem.*, 1968, **40**, 1086.
6. L. A. Trudell and D. F. Boltz, *Anal. Letters*, 1970, **39**, 465.
7. G. F. Kirkbright and J. H. Yoe, *Talanta*, 1964, **11**, 415.
8. V. Djurkin, G. F. Kirkbright, and T. S. West, *Analyst*, 1966, **91**, 89.
9. R. F. Milton, *ibid*, 1951, **76**, 431.
10. C. E. P. Jeffreys and E. H. Swift, *J. Am. Chem. Soc.*, 1932, **54**, 3219.
11. H. Kaiser, *Anal. Chem.*, 1970, **42** (April Issue), 26A.

Talanta, 1972, Vol. 19, pp. 45 to 49. Pergamon Press. Printed in Northern Ireland

STUDIES ON POTASSIUM CHLORATE AS A PRIMARY OXIDIMETRIC REAGENT

C. RADHAKRISHNA MURTY and G. GOPALA RAO
Department of Chemistry, Andhra University, Waltair, India

(*Received* 30 *October* 1970. *Revised* 1 *July* 1971. *Accepted* 23 *August* 1971)

Summary—Conditions have been established for the use of potassium chlorate as a primary oxidizing agent in the direct titration of vanadium(III), tin(II) and titanium(III) with visual or potentiometric end-points.

POTASSIUM CHLORATE is available in high purity, some commercial grades assaying as high as 99·7%, but has found little use as a titrimetric reagent. It may function in acid solution either as a 5- or a 6-electron oxidant, the redox potentials being 1·47 and 1·45 V respectively, but is relatively inert as an oxidant in dilute acid solution. The rate of reaction of potassium chlorate even with substances of very low redox potentials such as tin(II) and titanium(III) is very low. Potassium chlorate furnishes an excellent example of a reagent the practical function of which as an oxidant is governed more by kinetic considerations than by thermodynamics. We have now found conditions under which potassium chlorate can be used as a convenient oxidant for direct titrimetric determination of vanadium(III), tin(II) and titanium(III).

Potassium iodate is kinetically a more facile oxidant than bromate and chlorate, although thermodynamically the order of reactivity should be bromate > chlorate > iodate, as indicated by the redox potentials.[1] The kinetic order of reactivity, iodate > bromate > chlorate is exemplified by the reaction with iodide. The speed of the reaction increases with increasing hydrogen ion concentration. Iodate ion reacts rapidly and completely at a much lower hydrogen concentration than does bromate. According to Kolthoff and Hume,[2] at pH 4–5 the iodate–iodide reaction is complete whereas the bromate reaction is negligibly slow and iodate can be determined in the presence of bromate at pH 4. The bromate reaction requires a hydrochloric acid concentration of at least 0·5*M*, though catalysts such as ammonium molybdate can be used at lower acidity. According to Ferrey[3] the chlorate reaction is rapid only when the hydrochloric acid concentration is 7·5*M*, but under these conditions iodide is oxidized by aerial oxygen anyway so the reaction is not useful for analytical purposes.

More recent kinetic studies confirm these findings.[4] The variation in the rate of oxidation with the atomic number of the halogen is presumably related to the strength of the oxygen–halogen bond and the ability of the halogen atom to achieve an increased co-ordination number in the transition state. The halate oxidation rates show a similarity to the rates of halate oxygen-exchange reactions, iodate giving rapid exchange with water at room temperature even in neutral solution, whereas bromate and chlorate exchange slowly.[5] The rate of oxygen exchange of bromate and chlorate with water is dependent on the square of the hydrogen ion concentration, and is faster in D_2O than in H_2O. This suggests that protonation occurs rapidly and reversibly before the rate-determining step.

$$2H^+ + ClO_3^- \rightleftharpoons H_2ClO_3^+$$

$$X^- + H_2ClO_3^+ \rightarrow \text{products.}$$

The rates of oxidations with chlorate, bromate and iodate are largely dependent on the hydrogen ion concentration of the medium, showing either first-order or second-order dependence. The reaction of chlorate with a halide follows the rate law

$$\frac{-d[X^-]}{dt} = k[ClO_3^-][X^-][H^+]^2.$$

The protons are used in production of water from the halate, and this may occur by an S_N1 mechanism such as

$$ClO_3^- + H^+ \rightleftharpoons HOClO_2$$

$$HOClO_2 + H^+ \rightarrow ClO_2^+ + H_2O$$

$$ClO_2^+ + X^- \rightarrow XClO_2$$

or an S_N2 mechanism such as

$$ClO_3^- + 2H^+ \rightleftharpoons H_2OClO_2^+$$

$$H_2OClO_2^+ + X^- \rightarrow XClO_2 + H_2O.$$

It appears that on the addition of hydrogen ions the oxy-anions are converted into less stable forms which can easily react with other chemical entities. Another fact of importance to the rates of reactions involving oxy-anions is the oxidation state of the central atom. The rates of replacement reactions for a lower oxidation state are faster than for a higher oxidation state. Thus the rates of perchlorate reactions in aqueous solution are extremely slow, those of hypochlorite very rapid, and those of chlorite and chlorate are intermediate.

Taking into account these theoretical considerations, we have been able to establish conditions under which potassium chlorate reacts very rapidly with vanadium(III), tin(II) and titanium(III). The reactions of chlorate with vanadium(III), tin(II) and titanium(III) become fast enough for titration purposes at very high mineral acid concentrations; under the prescribed conditions the reactions have been found to be stoichiometric according to the equation:

$$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$$

EXPERIMENTAL

Solutions

Potassium chlorate, 0·1*N*. Prepared from *pro analysi* reagent (Merck) dried at 100°; standardized as described by Vogel.[6]

Vanadium(III), 0·1*N*. Prepared by cathodic reduction of 0·1*N* sodium vanadate solution in 0·5*N* sulphuric acid.[7] Kept in a reservoir fitted with an automatic burette, and stored under carbon dioxide. The solution contains mostly vanadium(III) and a little vanadium(IV) and is standardized according to Murty and Rao.[8]

Tin(II) chloride and titanium(III) chloride, 0·1*N*. Prepared in hydrochloric acid, stored and standardized by the usual methods.

Titration of vanadium(III)

Preliminary studies showed that only 5–7*M* hydrochloric acid is a suitable medium for the potentiometric titration, but the potential requires 5 min to stabilize, and the end-point inflection is poor. However, addition of 0·3 ml of 0·1*M* iron(III) sulphate in a titration volume of 50 ml gave not only potential stabilization within 1 min, but also gave a good inflection in the titration curve. Phosphoric acid, osmium tetroxide and potassium iodide did not have this beneficial effect. A carbon dioxide atmosphere was used, owing to the instability of vanadium(III) solutions in air. Seven titrations gave a value of 6·01 ± 0·02 moles of vanadium(III) oxidized per mole of potassium chlorate used, confirming the stoichiometry.

Procedure

Take 27–31 ml of concentrated hydrochloric acid and 15–11 ml of distilled water in a 150-ml Pyrex titration cell so as to keep the overall acidity 6–7*M* on final dilution to 50–60 ml. The cell is fitted with a 5-holed rubber stopper accommodating the platinum electrode, porous salt bridge, microburette, and inlet and outlet tubes for carbon dioxide. A thick platinum wire is used as indicator electrode and a saturated calomel electrode as reference. Before the titration pass carbon dioxide through the mixture for 5–10 min to expel dissolved oxygen. Add a 3–6 ml portion of vanadium(III) solution to the titration vessel and pass carbon dioxide while the mixture is stirred by a magnetic stirrer Add 0·3 ml of 0·1*M* iron(III) sulphate. Titrate with 0·1*N* potassium chlorate, noting the potentials with a wait of 1 min after each addition of the titrant. The potential jump at the equivalence point is 200–270 mV per 0·04 ml of 0·1*N* potassium chlorate. Some representative results are presented in Table I

TABLE I.—TITRATION OF VANADIUM(III) WITH POTASSIUM CHLORATE

Condition	Vanadium(III), *mmole*	
	Taken	Found
Potentiometric,	0·2418	0·2424
6*M* HCl,	0·3650	0·3660
inert atmosphere	0·5024	0·5008
	0·5244	0·5230
Indicator	0·5352	0·5337
Methyl Orange,	0·5588	0·5571
6*M* HCl,		
inert atmosphere	0·5816	0·5840
	0·2876	0·2888

Visual titration

Methyl Orange can be used as redox indicator for this titration. Ferroin, diphenylbenzidine, diphenylaminesulphonate, Methyl Red and other dyes did not prove useful. More catalyst is necessary, at least 1 ml of 0·1*M* iron(III) sulphate for 50–60 ml of titration mixture. With a smaller amount of catalyst the indicator is bleached before the equivalence point.

Take 27 ml of concentrated hydrochloric acid, 18 ml of distilled water, 1 ml of 0·1*M* iron(III) and 3 drops of 0·1% Methyl Orange solution in the titration cell, and pass carbon dioxide through for 5–10 min. Then add the vanadium(III), pass carbon dioxide while the mixture is stirred magnetically, and titrate with 0·1*N* potassium chlorate, rapidly in the beginning and slowly towards the equivalence point, where 20–25 sec should be allowed between additions of a drop of the reagent. The end-point is denoted by the disappearance of the red colour. The indicator correction is 0·06 ml to be deducted. The average relative error is ±0·4%.

Titration of tin(II)

Kulwarskaja[3] determined tin(II) with chlorate, but had to titrate the solution at boiling temperature. We titrate tin(II) potentiometrically with potassium chlorate at room temperature in hydrochloric, sulphuric or phosphoric acid media. Conditions have also been found for the visual titration, using Phenosafranine, Neutral Red, Methylene Blue and Naphthol Blue Black as indicators in hydrochloric acid medium, and ferroin as indicator in sulphuric acid medium. None of these indicators functions in phosphoric acid medium.

Potassium chlorate reacts with tin(II) rapidly when the acid concentration is >5*M* for hydrochloric acid, >6*M* for sulphuric acid, and >12*M* for phosphoric acid, but the stabilization of potentials is slow, especially in phosphoric acid, in the vicinity of the end-point (4–6 min in HCl, 3–6 min in H_2SO_4, 4–6 min in initial stages and 10–12 min in final stages in H_3PO_4). The potential breaks are ~500 mV/0·04 ml of titrant in HCl and H_2SO_4 media but only ~350 mV in H_3PO_4. The average relative error is ±0·2% in hydrochloric acid medium and ±0·4% in the other two media. Some representative results are presented in Table II.

Satisfactory visual titrations have been made in an inert atmosphere, with Methylene Blue or

TABLE II.—TITRATION OF TIN(II) WITH POTASSIUM CHLORATE

Conditions	Tin(II), *mmole*	
	Taken	Found
Potentiometric, 5–6*M* HCl	0·2345	0·2340
	0·2535	0·2530
	0·2836	0·2842
	0·3325	0·3335
Indicator Methylene Blue, 6–7*M* HCl	0·2468	0·2476
	0·3147	0·3139
	0·4055	0·4043
	0·5454	0·5470
Indicator Phenosafranine, 6–7*M* HCl	0·2104	0·2098
	0·3231	0·3243
	0·3766	0·3750
	0·4566	0·4578

Phenosafranine in 6–7*M* hydrochloric acid medium, Neutral Red in 7–8*M* acid and Naphthol Blue Black in 6–8*M* hydrochloric acid. It is within these limits of acidity that both the reduction of the dye by stannous chloride and the reoxidation of the leuco dye are fast. The indicator corrections are negligible. The average relative error is ±0·3%. Typical results are presented in Table II.

None of these indicators functions satisfactorily in sulphuric acid medium. Only ferroin works satisfactorily, although it does not do so in hydrochloric acid medium. It is used in 6–7*M* sulphuric acid, with the addition of 10 ml of phosphoric acid for 50 ml of titration mixture. The indicator correction is 0·07 ml for 2 drops of 0·01*M* ferroin.

Titration of titanium(III)

Titanium(III) can be titrated with potassium chlorate solution at room temperature, using Neutral Red or Phenosafranine as indicator, in 6–8*M* hydrochloric acid. The average relative error is ±0·3%. Some representative results are presented in Table III.

TABLE III.—TITRATION OF TITANIUM(III) WITH POTASSIUM CHLORATE

Conditions	Titanium(III), *mmole*	
	Taken	Found
Indicator Phenosafranine, 6–8*M* HCl, inert atmosphere	0·3324	0·3334
	0·4249	0·4237
	0·5950	0·5928
	0·7463	0·7452
Indicator Neutral Red, 6–8*M* HCl, inert atmosphere	0·3485	0·3474
	0·3842	0·3856
	0·5228	0·5238
	0·5719	0·5739

Zusammenfassung—Für die Verwendung von Kaliumchlorat als primäres Oxidationsmittel bei der direkten Titration von Vanadium(III), Zinn(II) und Titan(III) mit visueller oder potentiometrischer Endpunktsanzeige wurden die optimalen Bedingungen ermittelt.

Résumé—On a établi les conditions d'emploi du chlorate de potassium comme agent d'oxydation primaire dans le titrage direct des vanadium(III), étain(II) et titane(III) avec points de virage visuels ou potentiométriques.

REFERENCES

1. T. Moeller, *Inorganic Chemistry*, Asian Students Ed., p. 438. Asia Publishing House, Bombay, 1966.

2. I. M. Kolthoff and D. N. Hume, *Ind. Eng., Chem., Anal. Ed.*, 1943, **15**, 174.
3. G. J. W. Ferrey, *Quart. J. Pharm. Pharmacol.*, 1932, **5**, 405.
4. J. O. Edwards, *Chem. Revs.*, 1952, **50**, 455; *J. Chem. Educ.*, 1954, **31**, 270. L. A. Fedorova and E. A. Kanevskii, *Radiokhimiya*, 1962, **4**, 502; *Kinetika Kataliz*, 1962, 3, 332. L. T. Bugaenko, *Zh. Neorg. Khim.*, 1960, **5**, 1894. S. Dushman, *J. Phys. Chem.*, 1904, **8**, 453. K. J. Morgan, M. G. Peard and C. F. Cullis, *J. Chem. Soc.*, 1951, 1865. M. Wronska and B. Banas, *Bull. Acad. Polon Sci., Ser. Sci. Chim.*, 1965, **13**, 5.
5. T. C Hoering, R. C. Butler and H. C. Mcdonald, *J. Am. Chem. Soc.*, 1956, **78**, 4829.
6. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 313. Longmans, London, 1964.
7. G. G. Rao and L S. A. Dikshitulu, *Talanta*, 1963, **10**, 295.
8. B. V. S. R. Murty and G. G. Rao, *ibid.*, 1961, **8**, 426.
9. R. M. Kulwarskaja, *Z. Anal. Chem.*, 1932, **89**, 199.

Talanta, 1972, Vol. 19, pp. 51 to 57. Pergamon Press. Printed in Northern Ireland

A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COPPER IONS AND ITS APPLICATION TO THE CO-PRECIPITATION OF COPPER IN THE CRYSTALLIZATION OF SODIUM CHLORIDE*

A. GLASNER, S. SARIG, D. WEISS and M. ZIDON
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem,
Jerusalem, Israel

(*Received* 29 *March* 1971. *Accepted* 27 *June* 1971)

Summary—The molar absorptivity of the cyanide complexes $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, at their isosbestic wavelength (235 nm) is $1{\cdot}13 \times 10^3$ l.mole^{-1}.mm^{-1} and can be used for the quantitative determination of micro-amounts of copper in the ppm range. The determination of 1–10 μg of Cu^{2+} per g of NaCl, or 0·25–2·5 μg/ml, is described in detail. The co-precipitation of copper with NaCl crystallizing from aqueous solutions has been studied by this method.

CUPRIC CHLORIDE is readily converted, on addition of cyanide, into the cuprous cyanide complex even in a concentrated alkali metal halide solution.[1] The cuprous cyanides have a distinct absorption in the 225–240 nm region which can serve for the identification and quantitative determination of micro-amounts of copper. However, the shape and position of the absorption band are affected by the concentration of copper, by the concentration of cyanide, and by the ratio between them.

Glasner and Avinur[1] have found that in order to obtain a well-developed narrow band with its peak at about 235 nm it is necessary to add cyanide in some excess to the concentrated alkali metal chloride solutions containing the copper(II) ions. This excess was assumed to be at least 20 moles of cyanide per mole of copper. However, the quantitative determination of copper, especially at very low concentrations in the ppm range, was not satisfactory.

Baxendale and Westcott[2] found that a $6 \times 10^{-6}M$ solution of $K_3Cu(CN)_4$ shows an absorption band with a peak at 234 nm, which they attributed to the $Cu(CN)_2^-$ species. This peak shifted to longer wavelengths on addition of either free cyanide or sodium hydroxide, the shift being ascribed to the formation of $Cu(CN)_3^{2-}$; the four-co-ordinated complex may not be attainable at the low concentrations mentioned. Kappenstein and Hugel[3] convincingly proved that both $Cu(CN)_4^{3-}$ and $Cu(CN)_3^{2-}$ absorb strongly in the 225–240 nm region, having an isosbestic point at 235 nm. They determined the stability constant of the tetracyano complex

$$CN^- + Cu(CN)_3^{2-} \rightleftharpoons Cu(CN)_4^{3-} \qquad (1)$$

in *ca.* $2M$ sodium perchlorate solution.

This constant (418 ± 12 l.mole^{-1} at 25°) was found to be valid for solutions ranging from $0{\cdot}2M$ to $10^{-4}M$ copper, when the mole fraction of $Cu(CN)_3^{2-}$ varied from 0·1 to 0·96 respectively, and the amount of other species present was negligible. They excluded from their study solutions of lower copper concentration, in the range $1\text{–}5 \times 10^{-5}M$, in which the calculated mole fraction of $Cu(CN)_3^{2-}$ would be above 0·96, and its dissociation to a lower co-ordinated complex most probable.

---

* This work was supported by an NBS Grant No. (G)-86

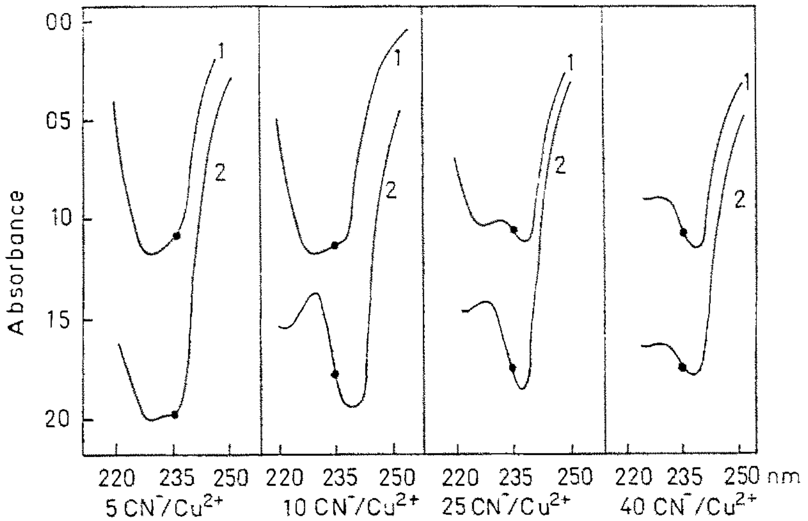


FIG. 1.—The absorption spectra of copper cyanide solutions of varying CN^-/Cu^{2+} ratio. Series 1 contained 1·5 μg Cu^{2+}/ml; series 2 contained 2·5 μg Cu^{2+}/ml.

As the range of copper concentrations of analytical interest to us coincided with the range excluded by Kappenstein and Hugel,[3] the prime aim of this work was to determine the excess of cyanide needed in order to keep the mole fraction of $Cu(CN)_3^{2-}$ sufficiently low to prevent further dissociation which would affect the value of the molar absorptivity at the isosbestic point.

A number of different values of the stability constant required for such a computation can be found in the literature;[2–6] virtually all of them are "concentration constants" determined at different ionic strengths. The reported values vary within an order of magnitude.[3] Experimental determination of the cyanide excess needed was therefore indicated.

EXPERIMENTAL

The test solutions contained 2·5 g of alkali metal halide (J. T. Baker, "Baker-Analyzed") per 10 ml of solution, and appropriate amounts of copper [1–10 μg of copper(II) per g of alkali metal halide]. Potassium cyanide solution was added in the desired excess before the flask was filled to the mark. A pure alkali metal halide solution of identical concentration, but without added copper and cyanide, served as the reference. The copper stock solution was prepared from $CuSO_4.5H_2O$ (J. T. Baker, "Baker-Analyzed") and its copper content was ascertained by electrolysis.

In order to determine the effect of other cations present, the chlorides of Zn^{2+}, Mn^{2+}, Cd^{2+}, Fe^{2+}, Ni^{2+}, Fe^{3+} and Au^{3+} were used.

The analytical method was applied to a series of sodium chloride samples crystallized by evaporation at 65° from solutions containing 490 or 980 μg of copper(II) per g of sodium chloride.

RESULTS

Figure 1 shows the absorption spectra of two series of copper solutions and their variation with the mole ratio CN^-/Cu^{2+}. All the solutions contained 0·25 g of sodium chloride and 1·5 or 2·5 μg of copper per ml, and 40-mm cells were used. With low CN^-/Cu^{2+} ratios the absorption bands are broad and ill-defined. As this ratio increases, a well-developed band, with a peak at 237 nm, reveals itself and the absorbance at 235 nm, the isosbestic point, is the same for equal copper concentrations, irrespective of the cyanide excess. Also, the greater the concentration of the copper

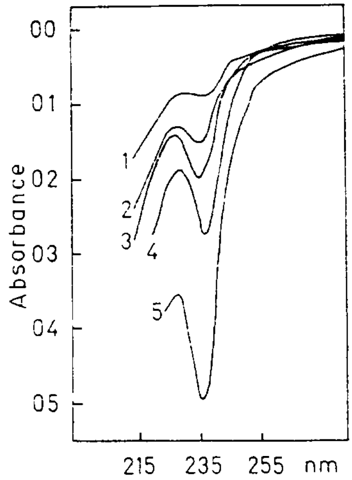


FIG. 2.—Absorption spectra of copper cyanide in NaCl solutions. Composition of solutions 1–5 was as given in Table I.

the smaller the ratio at which this constant value is attained; a tenfold molar ratio was sufficient for the solutions containing 2·5 μg of copper per ml.

Similarly, it has been established that solutions containing 10 μg of cyanide and 0·25 μg of copper per ml (*i.e.* 1 ppm of copper in the sodium chloride), will give the right band shape for a quantitative determination. This is equal to a mole ratio CN^-/Cu^{2+} of nearly 100, and hence 10 μg of cyanide were added per ml of test solution in the following experiments. The spectra obtained with varying amounts of copper (0·25–2·5 μg/ml) added to sodium chloride solutions (2·5 g/10 ml, weighed out separately) are recorded in Fig. 2 (10-mm cells were used). The shape of the absorption curves is satisfactory, but a plot of the absorbance values does not extrapolate to the origin, indicating the presence of 0·7 μg of Cu^{2+} per g of sodium chloride on the average.

As the copper content of the sodium chloride may vary from sample to sample, even if taken from the same bottle,[7] the series of measurements was repeated with solutions of similar composition, but the sodium or potassium chloride was taken by pipette from a single stock solution. The results are recorded in Table I.

Assuming that both salts were initially contaminated by a small amount of copper, we calculate the molar absorptivity as $1{\cdot}13 \times 10^3$ l.mole^{-1}.mm^{-1}, in close agreement

TABLE I.—THE ABSORBANCE OF COPPER CYANIDE SOLUTIONS AT THE ISOSBESTIC POINT, 235 nm

Cu^{2+}, *μg/ml*	Absorbance at 235 nm NaCl	Absorbance at 235 nm KCl
0·25	0·050	0·050
0·50	0·095	0·095
1·00	0·190	0·180
1·50	0·270	0·270
2·50	0·450	0·450

Cell path = 10 mm. All solutions contained 0·25 g of alkali metal chloride and 10 μg of cyanide per ml.

TABLE II.—THE ABSORBANCE OF 2·69 μg OF Cu^{2+}/ml, CYANIDE COMPLEXES IN NaCl SOLUTION, IN THE PRESENCE OF VARIOUS CATIONS, MEASURED AT 235 nm. EXPECTED ABSORBANCE VALUE: 0·483

Foreign cation	Au^{3+}	Mn^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Fe^{3+}
Absorbance	0·24	0·470	0·515	0·495	0·450	0·477
Deviation, %	−50	−2·7	+6·6	+2·5	−6·8	−1·2

with the values recorded in the literature[1–3] for different salt solutions and ionic strengths. Further, we note that the samples of chlorides used contain only about 0·1 ppm copper.

The influence of a number of cations on the estimation of copper by the proposed method was also investigated. Table II gives some of the absorbance readings of a solution containing 2·69 μg of copper and 0·25 g of sodium chloride per ml, in the presence of 10 μg of the ions listed, or 2·5 μg per ml in the case of nickel and iron(III). The expected absorbance of the pure solutions, without the foreign ions, is 0·483. It may be observed that only gold ions interfere seriously. The spectrum indicated the formation of the $[Au(CN)_2]^-$ complex, which consumed a good part of the excess of cyanide ions required for the formation of the $[Cu(CN)_3]^{2-}$ species. Adding a larger surplus of cyanide ions does not help, as the absorption bands overlap. This measure was adopted in the case of the nickel and iron(III) ions; the latter solutions contained 20 μg of cyanide per ml. Under these conditions both nickel and copper could be determined simultaneously. Small amounts of iron(II) ions appear to be totally oxidized to iron(III), probably by dissolved oxygen.

The deviations, indicated in Table II, from the expected value are due to the sum of the experimental errors as well as to the inhomogeneous distribution of the copper ions in the sodium chloride sample. The presence of some copper ions in the zinc and cadmium chlorides used is also suspected.

Several potassium and sodium chloride products were analysed for copper content by the proposed spectrophotometric method; 2 μg of Cu^{2+} per g of salt were initially added to each of the test solutions, in order to improve the precision of the measurements. Copper may be determined in other "pure" salts in a similar manner, unless the solution absorbs light appreciably in the spectral range 230–240 nm. For example, the method was not applicable to bromide solutions.

Our attempts to determine copper by atomic-absorption spectroscopy in these salts, or in other copper-doped samples, failed as the readings were completely irreproducible and non-linear.

Recommended procedure

Test solution. Dissolve 25 g of solid sample in 80 ml of triply distilled water. Filter off foreign particles.

Reagents. Potassium cyanide solution, 0·26 g/l. If cyanide-complexing cations are present, or if the copper content of the final test solution is greater than 2·5 μg/ml, a proportionately more concentrated solution should be prepared.

Standards. Copper range 2·5–25 mg/l. Triply distilled water throughout. Mix 8 ml of test solution with 1 ml of reagent and 1 ml of water (or standard copper solution) giving a total of 10 ml. Transfer the solution to the photometric cell and record the absorbance at 235 nm, using 8·0 ml of test solution + 2·0 ml of water in the reference cell. If the spectrum does not reveal a distinct band with a peak at 237 nm, use a more highly concentrated cyanide solution. If the copper content of the test solution is low (about 0·25 μg/ml or less), add 1 ml of a standard copper solution.

The co-precipitation of copper with crystallizing sodium chloride

The cyanide method was applied to the estimation of the amount of copper in fractions of sodium chloride crystallized by evaporating a solution at constant temperature, 65 ± 1°, and constant pressure, 20 mbar. The results of two series of experiments are given in Table III: 126 g of pure recrystallized sodium chloride were dissolved in 360 g of water, with 0·98 and 0·49 mg of copper per g of sodium chloride added in the two series respectively. The Pyrex glass vessel containing the solution was immersed in a large oil-bath, and the solution evaporated by continuous regulated pumping. The water vapour was condensed in a cold trap, where its volume or weight could be determined. After fixed intervals the crystallized salt was filtered off by suction through a sintered glass filter. A few ml of water were added to the filtered supersaturated solution and the fractional crystallization was continued. The filtered crystals were thoroughly washed with saturated sodium chloride solution to remove all adhering copper-rich solution, weighed after suction, dried at 130° and then re-weighed.

TABLE III.—AMOUNT OF COPPER IONS CO-PRECIPITATED IN CONSECUTIVE FRACTIONS OF NaCl CRYSTALLIZED FROM AN EVAPORATING AQUEOUS SOLUTION AT 65°C

Fraction	$\frac{\mu g\ Cu^{2+}}{g\ NaCl}$	NaCl crystd. X', g	NaCl in solution X_H, g	Cu co-ppted Y', μg	$\ln [X_H/(X_H - X')]$	$10^3 \times R$
Starting material	980*	—	126·0		—	—
1	5·29	34·16	126·0	185·0	0·3162	0·585
2	7·04	7·70	90·0	55·3	0·0893	0·619
3	7·37	6·80	80·9	51·1	0·08765	0·583
4	12·40	16·93	72·7	214·2	0·2651	0·808
Starting material	490†	—	126·0	—	—	—
1	4·84	15·21	126·0	75·1	0·1286	0·584
2	4·25	14·17	109·1	61·4	0·1391	0·442
3	6·50	14·93	93·2	99·0	0·1746	0·567
4	7·09	8·77	76·4	63·4	0·1219	0·520
5	7·60	11·13	65·9	86·3	0·1850	0·466
6	18·10	13·30	52·9	246·6	0·2896	0·851
7	16·10	8·02	37·8	131·7	0·2385	0·552

* Total Cu present in initial solution was 0·1225 g.

† Total Cu present in initial solution was 0·0612 g.

It may be seen that the copper content (μg of Cu^{2+}/g of NaCl) of the first fraction is only 0·5–1·0% of that of the dissolved salt, *i.e.*, co-precipitation is largely independent of the copper concentration. However the copper content of the crystallized fractions increases in an inverse proportion to the amount of sodium chloride in the solution.[8] The latter observation is expressed by the equation $Y' = R \ln [X_H/(X_H - X')]$, where Y' is the total amount of copper co-precipitated by each fraction, R is a constant, X_H is the weight of sodium chloride in the solution, and X' is the weight of each fraction of salt. The fluctuations in the R values are rather small, considering the experimental difficulties involved. Two exceptionally high values, one in each series, are thought to be due to incomplete washing of these crystallized fractions, and the analytical method appears to be fairly satisfactory.

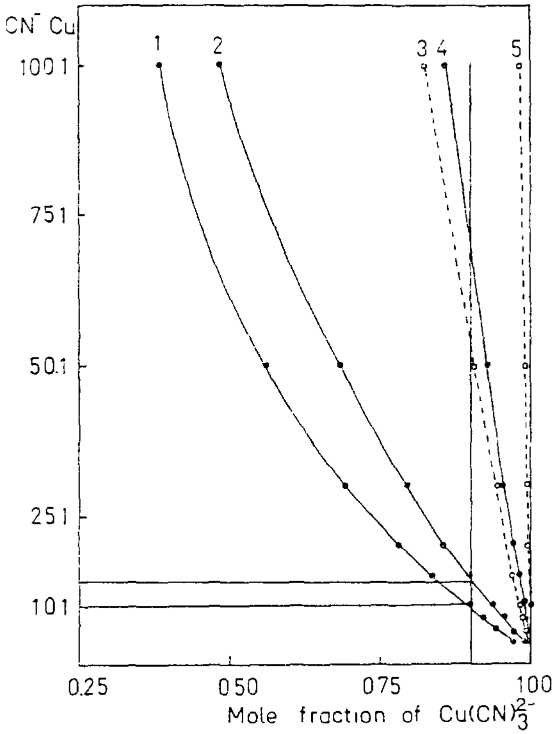


FIG. 3.—Calculated mole fraction of $[Cu(CN)_3]^{2-}$ as a function of the CN^-/Cu^{2+} ratio in the solution.
Assumed concentration of copper: *1*, *3*—2·5 μg/ml; *2*, *5*—1·5 μg/ml; *4*—0·25 μg/ml.
——$K = 418$; ---$K = 55$.

DISCUSSION

It has been proved experimentally that Beer's law is valid for the absorbance of the cyanide complexes $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ at the isosbestic wavelength 235 nm, in the copper concentration range of 0·25–2·5 μg/ml, if a sufficient excess of cyanide ions has been added to the solution. Our results are in good agreement with those of Kappenstein and Hugel.[3] These authors stated that if the mole fraction of the tricyano complex in the equilibrium equation (1) is calculated to be larger than 0·96 of the total copper concentration then the isosbestic point ceases to be reliable, because of the formation of complexes with lower co-ordination numbers. In Fig. 3 we plot the calculated mole fraction of the tricyano complex for three different concentrations of copper: 0·25, 1·5 and 2·5 μg/ml, as a function of the CN^-/Cu^{2+} mole ratio. The stability constants $K = 418$ from Ref. 3 and $K = 55$ from Ref. 2 (broken line) are used for these calculations. The mole fraction 0·90 of $[Cu(CN)_3]^{2-}$ is indicated by straight lines. This lower value (0·90) was adopted as an analytical safety margin. Comparison of Figs. 1 and 3 confirms the higher value of the two stability constants tested, and indicates that 0·25 μg Cu^{2+}/ml should be readily determinable in the presence of a minimum of a 70-fold excess of cyanide ions. However, the cyanide method would not be applicable to the determination of copper at lower concentrations.

No other metal ions except gold were found to interfere with the estimation of copper by the cyanide method. A larger excess of cyanide ions should however be added in the presence of cations giving stable cyanide complexes. In the procedure given here, a minimum concentration of cyanide was proposed so as to preclude the possibility of complications due to contamination.

The cyanide method was applied to a study of the co-precipitation of copper with sodium chloride crystallizing from aqueous solutions. Table III proves that the co-precipitation is largely independent of the concentration of copper ions in the solution or the amount of salt crystallized; it is inversely proportional to the amount of sodium chloride in the solution and can be expressed by an appropriate constant *R*. The *R* value of copper in sodium chloride is about $0{\cdot}56 \times 10^{-3}$, slightly less than that of calcium and magnesium ions.[9]

Zusammenfassung—Der molare Extinktionskoeffizient der Cyanidkomplexe $[Cu(CN)_3]^{2-}$ und $[Cu(CN)_4]^{3-}$ beträgt bei ihrer isosbestischen Wellenlänge (235 nm) $1.13{\cdot}10^3$ l mol^{-1} mm^{-1}; dies kann zur quantitativen Bestimmung von Mikromengen Kupfer im ppm-Bereich verwendet werden. Die Bestimmung von 1–10 μg Cu^{2+} pro g NaCl oder 0·25–2·5 $\mu g/ml$ wird in Einzelheiten beschrieben. Die Mitfällung von Kupfer beim Auskristallisieren von NaCl aus wäßrigen Lösungen wurde mit diesem Verfahren untersucht.

Résumé—Le coefficient d'absorption moléculaire des complexes du cyanure $[Cu(CN)_3]^{2-}$ et $[Cu(CN)_4]^{3-}$, à la longueur d'onde isobestique (235 nm) est de 1,13 × 10^3 l.mol.$^{-1}$ mm^{-1} et il peut être utilisé pour la détermination quantitative de micro-quantités de cuivre dans le domaine du ppm. On décrit en détail le dosage de 1–10 μg de Cu^{2+} par g de NaCl, ou de 0,25–2,5 $\mu g/ml$. On a étudié par cette méthode la coprécipitation du cuivre avec NaCl cristallisant de solutions aqueuses.

REFERENCES

1. A. Glasner and P. Avinur, *Talanta*, 1964, **11**, 761.
2. J. H. Baxendale and D. T. Westcott, *J. Chem. Soc.*, 1959, 2349.
3. C. Kappenstein and R. Hugel, *Rev. Chim. Minerale*, 1969, **6**, 1107.
4. R. P. Penneman and L. H. Jones, *J. Chem. Phys.*, 1956, **24**, 293.
5. H. P. Rothbaum, *J. Electrochem. Soc.*, 1957, **104**, 682.
6. P. Estrade, D.Sc. Thesis, Strasbourg, No. 177 (1966).
7. S. Sarig, A. Glasner, M. Zidon and D. Weiss, *Talanta*, 1969, **16**, 1488.
8. A. Glasner and J. Kenat, *J. Cryst. Growth*, 1970, **6**, 135.
9. A. Glasner, S. Skurnik-Sarig and M. Zidon, *Israel J. Chem.*, 1969, **7**, 649.

Talanta, 1972, Vol. 19, pp. 59 to 63. Pergamon Press. Printed in Northern Ireland

AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDIZING AGENT—V*

TITRIMETRIC DETERMINATION OF ARSENIC(III) AT ROOM TEMPERATURE

G. Gopala Rao, K. S. Murty and Muralikrishna Gandikota
Department of Chemistry, Andhra University, Waltair, India

(*Received* 16 *March* 1971. *Accepted* 20 *August* 1971)

Summary—Conditions have been established for the accurate titration of arsenic(III) with ammonium hexanitratocerate(IV) at room temperature in sulphuric, nitric and hydrochloric acid media, using suitable catalysts, and ferroin as indicator.

CERIUM(IV) SULPHATE in sulphuric acid medium is used for titration of arsenic(III), consequent on the work of Willard and Young[1,2] and Gleu,[3] and is nowadays often prepared from pure ammonium hexanitratocerate(IV). It would be an advantage if the ammonium hexanitratocerate(IV) could be used directly, especially as it is claimed to be of fixed composition and obtainable in high purity. Willard and Young[2] stated that arsenic(III) can be accurately determined in 3·0–4·2*M* hydrochloric acid with cerium(IV) sulphate at 50°, using iodine monochloride as catalyst and ferroin as indicator, but the procedure is rather inconvenient. Gleu[3] used three drops of 0·01*M* osmium tetroxide as catalyst and ferroin as indicator in about 0·5*N* sulphuric acid medium, but even then the oxidant should be added very slowly near the end. It is interesting that ferriin, the oxidized form of the indicator, is not readily reduced by arsenious acid; even in the presence of osmium catalyst only a faint red colour appears.

We have now established conditions for the rapid and accurate titration of arsenic(III) in 1–2*M* hydrochloric acid or 1–1·5*M* nitric acid, or 0·5–1·0*N* sulphuric acid at room temperature with ammonium hexanitratocerate(IV), using ferroin as indicator and a trace of iodine as catalyst. The titration can be done very rapidly even at the end-point, which is deemed to have been reached if the ferroin colour does not recur within 30 sec of the addition of the last fraction of a drop of the oxidant. Potassium iodide or iodate or iodine monochloride can also be used as catalysts, but corrections have to be made for the first two. At higher acid concentrations the results will be low by 0·05–0·1 ml of 0·1*M* cerate unless the titrations are carried out slowly towards the end. This is due to the slower reduction of ferriin by arsenic(III) at higher acid concentrations. The indicator correction is negligible in titrations with 0·1*M* cerium(IV) nitrate. With more dilute solutions of the oxidant indicator corrections are necessary.

A large number of titrations with varied acid concentrations showed that satisfactory conditions for the titration of arsenic(III) with ammonium hexanitratocerate(IV) with a potentiometric end-point are: (1) 1*N* sulphuric acid medium with trace amounts of iodide, iodine or iodine monochloride as catalyst, (2) 1*M* nitric acid with

---

* Part IV: *Talanta* 1964, **11**, 955.

0·1*M* potassium bromide or $10^{-5}M$ potassium iodide, $10^{-5}N$ I_2 or $10^{-6}M$ ICl as catalyst, (3) 1*M* hydrochloric acid with 0·1*M* potassium bromide or $10^{-5}M$ potassium iodide or $10^{-5}M$ iodine as catalyst. A negative correction has to be applied when potassium iodide is used, especially when working with dilute solutions of cerium(IV) nitrate.

Bromide failed to catalyse the reaction in sulphuric acid medium, but was effective at concentrations >0·1*M* in nitric or hydrochloric acid medium. In titrations using the bromide catalyst the potential break at the end-point is invariably much lower than in titrations using iodide, iodine or iodine monochloride catalyst in all the acid media tried. Moreover bromide is required at a much higher concentration than iodide. For these reasons the procedures using the iodine-based catalysts are recommended.

Some representative results are presented in Table I.

TABLE I.—TITRATION OF ARSENIC(III) AT ROOM TEMPERATURE WITH AMMONIUM HEXANITRATOCERATE(IV)

Medium	Arsenic(III) *mmole*		
	Taken	Found	Relative error %
1*M* HCl	0·2200	0·2194	−0·3
Ferroin indicator	0·1650	0·1645	−0·3
	0·1140	0·1137	−0·3
	0·0865	0·0862	−0·4
	0·0390	0·0388	−0·5
1*M* HNO_3	0·3500	0·3500	0·0
Ferroin indicator	0·2150	0·2147	−0·1
	0·1600	0·1600	0·0
	0·1250	0·1252	+0·2
	0·1050	0·1052	+0·2
	0·0800	0·0802	+0·3
	0·0650	0·0648	−0·3
	0·0500	0·0502	+0·4
1·0*M* HNO_3 + 0·1*M* KBr	0·4060	0·4064	+0·1
Potentiometric	0·2775	0·2772	−0·1
	0·2300	0·2294	−0·3
	0·1000	0·0996	−0·4
1·0*M* HNO_3 + $10^{-5}M$ KI	0·4000	0·3995	−0·1
Potentiometric	0·2700	0·2702	+0·1
	0·1600	0·1595	−0·3
1·0*M* HCl + 0·1*M* KBr	0·8100	0·8102	0·0
Potentiometric	0·1500	0·1498	0·0
1·0*M* HCl + $10^{-5}M$ KI	0·4000	0·3992	−0·2
Potentiometric	0·3200	0·3196	−0·1

EXPERIMENTAL

Preparation of solutions

Ammonium hexanitratocerate(IV), 0·1*M*. Prepared in 1*M* nitric acid and standardized against arsenic(III).[4]

Sodium arsenite, 0·1*N*. Prepared from analytical grade arsenious oxide dried at 105–110° for 1 hr.

All other chemicals employed in this investigation were of analytical reagent quality. The nitric acid was heated long enough to drive off oxides of nitrogen, and stored in an amber-coloured bottle.

All solutions were prepared in demineralized water because of the high susceptibility of the cerium(IV)–arsenic(III) reaction to catalysis by trace impurities.

Apparatus

The potentiometric titration assembly is that described earlier.[5]

DISCUSSION OF RESULTS

Willard and Young titrated arsenic(III) with cerium(IV) sulphate in 3–4·2*M* hydrochloric acid at 50°, using 5–10 ml of 0·005*M* iodine monochloride as catalyst and ferroin as indicator. For successful potentiometric titration at room temperature they had to use 4·2*M* hydrochloric acid and at least 5 g of potassium bromide as the catalyst (per 100 ml of titrand). This corresponds to about 0·4*M* bromide. We observed that arsenic(III) can be titrated rapidly with ammonium hexanitratocerate(IV) in 1*M* hydrochloric acid at room temperature with lower catalyst concentrations. Under our conditions the formal redox potential of the Ce(IV)/Ce(III) couple is about 1·08 V. In 1·0*M* nitric acid medium the redox potential of the Ce(IV)/Ce(III) couple is very high, about 1·61 V, but a catalyst is still needed for rapid oxidation of arsenic(III). This is indeed interesting because the formal redox potential of Ce(IV)/Ce(III) in the presence of bromide falls to about 1·1 V. This result brings out the significant point that for a rapid reaction to occur between cerium(IV) and arsenic(III) the redox potential of the oxidant is not of such importance as is usually believed. It is the presence of environmental ions that matters.

The potentiometric titration of arsenic(III) with cerium(IV) is not possible without a catalyst in perchloric acid,[6] nitric acid, sulphuric acid or hydrochloric acid, in which the Ce(IV)/Ce(III) couple has formal redox potentials of about 1·7, 1·61, 1·44 and 1·28 V respectively, but is possible in the presence of 0·1*M* bromide catalyst. In 1*M* nitric acid or 1*M* hydrochloric acid medium sodium chloride can be used in place of bromide as catalyst, but the concentration required is very much higher (>4*M* is required). Iodide has an effective catalytic action at a very much lower concentration than bromide.

Our observations may be explained in terms of a substitution reaction giving hexahalocerate(IV) instead of hexanitratocerate. It appears that bromide displaces the nitrate from the complex more easily than chloride does. The mechanism of the catalytic effect of chloride or bromide may be explained as being due to electron transfer from the arsenic(III) to cerium(IV) *via* the halide ion. The halide ion may even be oxidized within the halide complex, and the resulting halogen atom oxidizes the arsenic(III):

$$\mathrm{Ce(IV)} + \mathrm{Cl^-} \rightarrow \mathrm{Ce(III)} + \mathrm{Cl^0} \qquad (1)$$

$$\mathrm{Cl^0} + \mathrm{As(III)} \rightarrow \mathrm{Cl^-} + \mathrm{As(IV)} \qquad (2a)$$

$$\mathrm{Cl^0} + \mathrm{As(IV)} \rightarrow \mathrm{Cl^-} + \mathrm{As(V)} \qquad (2b)$$

or

$$2\mathrm{Cl^0} + \mathrm{As(III)} \rightarrow 2\mathrm{Cl^-} + \mathrm{As(V)}. \qquad (3)$$

The transient formation of the unstable state As(IV) has been assumed by Csanyi,[7] and others. That electron transfer from arsenic(III) occurs *via* the halide ion is evident from the fact that bromide is effective at a much lower concentration than chloride. It is known that bromide is more rapidly oxidized than chloride by cerium(IV) nitrate. This mechanism also explains why cerium(IV) does not readily oxidize arsenic(III) in nitric acid or sulphuric acid media in the absence of a catalyst; nitrate and sulphate are already fully oxidized and cannot serve as electron transfer agents.

There are reports that in solutions of ammonium hexanitratocerate(IV) in <2*M* nitric acid, there may not be much of the cerium(IV) present in the complex anionic form, only free or hydrolysed and polymerized cerium(IV) ions being present. If that be the case a slight modification of the mechanism suggested above becomes necessary, invoking the work of Duke and Borchers.[8] They explained the kinetics of the oxidation of chloride by cerium(IV) by assuming the formation of chloro-complexes of the type $CeCl^{3+}$, $CeCl_2^{2+}$ *etc*, followed by:

$$CeCl_3^+ \rightarrow Ce^{3+} + Cl^- + Cl_2^- \qquad (4)$$

$$CeCl_2^{2+} \rightarrow Ce^{3+} + Cl_2^- \qquad (5)$$

The resulting Cl_2^- (or the Br_2^- from the bromide) may be assumed to oxidize arsenic(III) rapidly:

$$Cl_2^- + As(III) \rightarrow As(IV) + 2Cl^-. \qquad (6)$$

The mechanism of the action of iodide (iodine or iodine monochloride) appears to be somewhat different from that of bromide and chloride. Because iodide works at trace concentrations of the order of $10^{-5}M$ the mechanism may be believed to be truly catalytic and not necessarily involving any breaking of the complex nitratocerate. Both iodine and iodide may be converted by nitratocerate in nitric, sulphuric or hydrochloric acid medium into iodine(I) (as in iodine monochloride) which then acts as the catalyst:

$$As(III) + I(I) \rightarrow As(IV) + I^0 \qquad (7)$$

$$As(IV) + I(I) \rightarrow As(V) + I^0 \qquad (8)$$

$$I^0 + I^0 \rightarrow I_2 \qquad (9)$$

$$I^0 + Ce(IV) \rightarrow I(I) + Ce(III). \qquad (10)$$

This mechanism implies that if molecular iodine is formed according to reaction (9) the speed of oxidation of arsenic(III) would be retarded. Indeed we have observed that when the iodine monochloride concentration is increased beyond a certain limit the reaction becomes sluggish. In acid solution molecular iodine does not react with arsenic(III), because the As(III)/As(V) potential is pH dependent and increased by acidity, whereas that of the I^-/I_2 couple is not.

That the mechanism of catalytic action of iodine is somewhat different from that of chloride and bromide is also indicated by the fact that iodide is required as catalyst even in hydrochloric acid medium and has a pronounced catalytic action even in sulphuric acid medium where chloride has a negligible, and bromide a poor catalytic action; in sulphuric acid medium cerium(IV) forms very strong sulphate complexes which cannot be easily transformed into the chloro- and bromo-complexes unless very high concentrations of these ligands are added.

Résumé—On a établi des conditions pour le titrage précis de l'arsenic-(III) par l'hexanitratocérate(IV) d'ammonium à température ordinaire, dans des milieux acide sulfurique, acide nitrique et acide chlorhydrique, en utilisant des catalyseurs convenables et la ferroïne comme indicateur.

Zusammenfassung—Die Bedingungen für eine genaue Titration von Arsen(III) mit Ammoniumhexanitratocerat(IV) bei Zimmertemperatur in schwefelsaurer, salpetersaurer und salzsaurer Lösung unter Verwendung geeigneter Katalysatoren und Ferroin als Indikator wurden ermittelt.

REFERENCES

1. H. H. Willard and P. Young. *J. Am. Chem. Soc.*, 1928, **50**, 1372
2. *Idem*, *ibid.*, 1933, **55**, 3260.
3. K. Gleu, *Z. Anal. Chem.*, 1933, **95**, 305.
4. E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.*, 1930, **52**, 901.
5. G. G. Rao, K. S. Murty, and P. V. K. Rao, *Talanta*, 1963, **10**, 657.
6. G. F. Smith, *Cerate Oxidimetry*, G. F. Smith Chemical Co., Columbus, Ohio.
7. L. J. Csyani, *Disc. Faraday Soc.*, 1960, **29**, 146.
8. F. R. Duke and C. E. Borchers, *J. Am. Chem. Soc.*, 1955, **75**, 5186.

Talanta, 1972, Vol. 19, pp. 65 to 67. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Ammonium hexanitratocerate(IV) as an oxidizing agent—VI
Determination of chromium(III) through oxidation to chromium(VI) at room temperature

(*Received* 16 *March* 1971. *Accepted* 20 *August* 1971)

THE DETERMINATION of chromium(III) is of importance in the assay of ores, alloys, chromium-plating solutions and chrome-tanning liquors, and is usually done by oxidizing the chromium(III) to chromium(VI), which is then titrated after destruction of excess of oxidizing agent. The classical method of oxidizing chromium(III) with hydrogen peroxide or sodium peroxide in hot alkaline medium is subject to the defect that, if all the peroxide is not removed, it may reduce some of the chromic acid formed during acidification before titration of the chromic acid, or may react with the iodide added if an iodometric estimation is used. To facilitate the complete removal of hydrogen peroxide, Feigl *et al.*[1] added nickel nitrate after oxidation of chromium(III). Schulek and Szakacs[2] proposed destroying the excess of hydrogen peroxide by adding chlorine water and destroying excess of chlorine with cyanide. Willard and Young[3] boiled the chromium(III) with concentrated perchloric acid, cooled, added a known and excessive amount of ferrous ammonium sulphate, and back-titrated with permanganate. Smith[4] stated that some of the chromic acid formed may be reduced by hydrogen peroxide, which is a by-product of the reaction. Lynn and Mason[5] boiled the chromium(III) solution with an excess of 72% perchloric acid in a mixed medium of nitric acid and sulphuric acid containing silver nitrate as catalyst. This procedure also appears to be subject to Smith's criticism, as is evidenced by the high negative errors (−0·8%). Jarvenin[6] oxidized chromium(III) with excess of bromine in alkaline solution, acidified and boiled to remove the excess of bromine. Schulek and Dosza[7] stated that in this method some chromic acid is lost by reaction with bromide during expulsion of the bromine. To avoid this error they oxidized with excess of hypobromite in alkaline medium and removed the excess with phenol. In our opinion some chromic acid may react with phenol during acidification. Kolthoff and Sandell[8] oxidized with an excess of potassium bromate in dilute sulphuric acid containing phosphoric acid and manganous chloride, decomposing the excess by boiling with ammonium persulphate and hydrochloric acid. This process also involves some loss of chromic acid as chromyl chloride or by reaction with bromite. Willard and Young[9] oxidized chromium(III) by boiling with excess of cerium(IV) sulphate in sulphuric acid, and back-titrated the excess with oxalate, or nitrite.[10] Both procedures must be subject to some error caused by reduction of cerium(IV) in a boiling solution, as has been established in recent years. Van der Meulen[11] oxidizes with excess of potassium persulphate in the presence of zinc sulphate, sodium sulphate and silver nitrate, boils to destroy excess of persulphate, adds manganous sulphate and heats until the supernatant liquid is a clear yellow, filters through a sintered glass crucible, cools and determines the chromium(VI) iodimetrically. This procedure is time-consuming and requires too many chemicals, though it is accurate.

We have now made the interesting new observation that ammonium hexanitratocerate(IV) oxidizes chromium(III) in dilute nitric acid at room temperature rapidly and stoichiometrically. The optimum conditions are 0·5–1M nitric acid and 50–100% excess of the reagent for a reaction time of 10–15 min.

EXPERIMENTAL

Reagents

Ammonium hexanitratocerate (IV) solution, 0·1M. Prepared according to Smith *et al.*[12] and standardized with sodium oxalate (ferroin indicator or potentiometrically[13]).

Sodium oxalate solution, 0·1N. Sodium oxalate was dried at 120° for 2 hr, dissolved in doubly distilled water tested for freedom from heavy metal ions, and stored in an amber glass bottle.

Chrome alum solution, 0·1N. Standardized by the method of van der Meulen.[11]

All other solutions were prepared from chemicals of analytical reagent quality. Nitric acid was heated long enough to drive off any oxides of nitrogen present and then stored in an amber coloured bottle.

Procedure

To 3–8 ml of chromium (III) solution (∼ 0·1N) add a known and excessive amout of ammonium hexanitratocerate(IV) (6–16 ml of 0·1M), 10 ml of 5·0M nitric acid, dilute with water to 50 ml, and set aside for 15–20 min. Then titrate the unreacted cerium(IV) slowly with 0·1N sodium oxalate potentiometrically.[13] The potential break at the equivalence point is ∼ 400 mV per 0·1 ml of oxalate.

RESULTS AND DISCUSSION

The stoichiometry was confirmed by taking an aliquot of chrome alum solution, oxidizing, adding the calculated amount of sodium oxalate equivalent to the unreacted Ce(IV) nitrate, letting stand for 5 min, making 2N in acid by addition of sulphuric acid, and titrating the chromium(VI) with iron(II) solution, using barium diphenylaminesulphonate as indicator.

Typical results are given in Table I. The good agreement between the results affords proof of the stoichiometric oxidation of chromium (III) with ammonium hexanitratocerate (IV) to chromium (VI) at room temperature.

TABLE I

Chromium (III) taken, *mmole*	Chromium (III) found, *mmole*			
	Procedure	Relative error %	Iron (II) titration	Relative error %
0·0667	0·0664	−0·5	0·0665	−0·3
0·1000	0·1003	+0·3	0·1004	+0·4
0·1330	0·1327	−0·2	0·1328	+0·2
0·1687	0·1689	+0·1	0·1688	+0·1
0·1767	0·1762	−0·3	0·1760	−0·4
0·2000	0·1997	−0·2	0·1999	−0·1
0·2033	0·2031	−0·1	0·2034	0·0

Chemistry Department
Andhra University
Waltair, India

G. GOPALA RAO
K. S. MURTY
MURALIKRISHNA GANDIKOTA

Summary—A new method has been developed for the determination of chromium(III), depending on its oxidation to chromium(VI) at room temperature by treatment with 50–100% excess of ammonium hexanitratocerate(IV) in 1·0M nitric acid medium. The reaction is complete within 15 min. The unreacted cerium(IV) is titrated potentiometrically with sodium oxalate.

Zusammenfassung—Ein neues Verfahren zur Bestimmung von Chrom-(III) wurde entwickelt. Es beruht auf der Oxidation zu Chrom(VI) bei Zimmertemperatur mit einem 50–100%-igen Überschuß von Ammonium-hexanitratocerat(IV) in 1M salpetersäurer Lösung. Die Reaktion ist in 15 min abgeschlossen. Das nicht verbrauchte Cer(IV) wird potentiometrisch mit Natriumoxalat titriert.

Résumé—On a élaboré une nouvelle méthode pour le dosage du chrome-(III), basé sur son oxydation en chrome(VI) à température ordinaire par traitement avec un excés de 50–100% d'hexanitratocétate(IV) d'ammonium en milieu acide nitrique 1,0M. La reaction est complète en 15 mn. Le cerium(IV) qui n'a pas réagi est titré potentiométriquement à l'oxalate de sodium.

REFERENCES

1. F. Feigl, K. Klaufer and L. Weidenfeld, *Z. Anal. Chem.*, 1930, **80**, 5.
2. E. Schulek and M. Szakacs, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 457.
3. H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 48.
4. G. F. Smith, *Analyst*, 1955, **80**, 16; *cf. Perchloric Acid*, 4th Ed., G. F. Smith Chemical Co., Columbus, Ohio, 1946.
5. S. Lynn and D. M. Mason. *Anal. Chem.*, 1952, **24**, 1855.
6. K. K. Jarvenin, *Z. Anal. Chem.*, 1928, **75**, 1.

7. E. Schulek and A. Dosza, *ibid.*, 1931, **86**, 81.
8. I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 140.
9. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1929, **51**, 139.
10. *Idem*, *Trans. Electrochem. Soc.*, 1935, **67**, 347.
11. J. H. van der Meullen, *Rec. Trav. Chim.*, 1932, **51**, 369.
12. G. F. Smith, V. R. Sullivan and G. Frank, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 449.
13. G. G. Rao, K. S. Murty and P. V. K. Rao, *Talanta*, 1963, 10, 657.

Talanta, 1972, Vol. 19, pp. 67 to 71. Pergamon Press. Printed in Northern Ireland

A rapid automatic method for the determination of oxygen in organic substances, using coulometry at controlled potential

(*Received* 15 *July* 1971. *Accepted* 28 *August* 1971)

SINCE 1954 we have performed routine determinations of oxygen in organic substances according to the procedure of Unterzaucher.[1] The final step in this method is the following. The iodine which is formed by the reaction of carbon monoxide with anhydroiodic acid is collected in a tube containing 20% sodium hydroxide solution. Bromine in acetate buffer is then added to this solution and all iodine is oxidized to iodate. Excess of bromine is removed by addition of formic acid, and bromine vapour in the flask is flushed out with a stream of air for 1 min. Sulphuric acid and potassium iodide are then added and the iodine formed is titrated with 0·02*N* thiosulphate.

The final step thus involves several manual operations. Many authors have tried to make the procedure more or less automatic and some of these methods will be briefly described. Fraisse and Levy[2] convert the carbon monoxide into carbon dioxide and titrate this with hydroxide ion generated coulometrically. Kan-Ichi Nakamura *et al.*,[3] using a rather complicated procedure, oxidize the carbon monoxide to carbon dioxide which is then reacted with lithium hydroxide to produce water, which is driven off and determined coulometrically in a Pt–P_2O_5 cell of the Keidel type. The accuracy of this method is, however, not very satisfactory. Calmè and Keyser[4] continuously titrate the iodine formed, with thiosulphate solution, in a special cell. Those methods which use gas chromatography in the final step, either for determination of carbon monoxide or of carbon dioxide, do not usually give such good values as Unterzaucher's original method.

The method which is described here is based on the continuous reduction of the iodine formed to iodide, at controlled potential.

Since iodine has been extensively studied in connection with coulometric measurements, and since with the help of modern electronic instrumentation quantities of electricity can be determined with very high accuracy, this procedure is very attractive.

Apparatus

The oxygen apparatus which is described here has been in use for about two years and is in principle the same as that of Unterzaucher up to and including the anhydroiodic acid tube. The iodine vapour which is formed here is led by the nitrogen gas stream (10 ml/min) through the electrically heated glass tube *A* (Fig. 1) down into the electrolysis cell *B*, also of glass, which contains 5 ml of 2*M* sodium iodide and 5 ml of 2*M* sodium perchlorate. To prevent the temperature from rising, the electrolysis cell is surrounded by a glass jacket through which cooling water is led in at *C* and out at *D*. *E* is a rotating platinum electrode consisting of a circular Pt gauze (36-mesh), diameter about 35 mm, fixed at one end to a rotating Teflon-coated shaft. The shaft rotates at about 400 rpm. *F* is a calomel reference electrode (Radiometer K 401). Electrolyte can be added to and removed from the cell through the hole stoppered by *G*. The nitrogen can leave the cell *via* a small hole in *G*. *H* is a circular Haldenwanger clay filter, diameter about 15 mm, fixed to the cell with special Haldenwanger cement. The anode, *K*, consists of a platinum gauze (36 mesh, 20 × 30 mm). The anode compartment contains 2*M* sodium perchlorate.

The platinum electrode, *E*, is connected *via* a mercury contact at the upper end of the rotating shaft with the positive input of an operational amplifier in a potentiostat of exactly the same construction as described by Karlsson and Karrman.[5] The reference electrode, *F*, is connected to the negative input of the operational amplifier, and the anode, *K*, to the output. The potential of the working electrode is always − 100 mV *vs.* the calomel electrode. The temperature of the tube *A* through which the iodine vapour is led from the anhydroiodic acid tube down to the working

7. E. Schulek and A. Dosza, *ibid.*, 1931, **86**, 81.
8. I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 140.
9. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1929, **51**, 139.
10. *Idem*, *Trans. Electrochem. Soc.*, 1935, **67**, 347.
11. J. H. van der Meullen, *Rec. Trav. Chim.*, 1932, **51**, 369.
12. G. F. Smith, V. R. Sullivan and G. Frank, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 449.
13. G. G. Rao, K. S. Murty and P. V. K. Rao, *Talanta*, 1963, 10, 657.

Talanta, 1972, Vol. 19, pp. 67 to 71. Pergamon Press. Printed in Northern Ireland

A rapid automatic method for the determination of oxygen in organic substances, using coulometry at controlled potential

(*Received* 15 *July* 1971. *Accepted* 28 *August* 1971)

SINCE 1954 we have performed routine determinations of oxygen in organic substances according to the procedure of Unterzaucher.[1] The final step in this method is the following. The iodine which is formed by the reaction of carbon monoxide with anhydroiodic acid is collected in a tube containing 20% sodium hydroxide solution. Bromine in acetate buffer is then added to this solution and all iodine is oxidized to iodate. Excess of bromine is removed by addition of formic acid, and bromine vapour in the flask is flushed out with a stream of air for 1 min. Sulphuric acid and potassium iodide are then added and the iodine formed is titrated with 0·02*N* thiosulphate.

The final step thus involves several manual operations. Many authors have tried to make the procedure more or less automatic and some of these methods will be briefly described. Fraisse and Levy[2] convert the carbon monoxide into carbon dioxide and titrate this with hydroxide ion generated coulometrically. Kan-Ichi Nakamura *et al.*,[3] using a rather complicated procedure, oxidize the carbon monoxide to carbon dioxide which is then reacted with lithium hydroxide to produce water, which is driven off and determined coulometrically in a Pt–P_2O_5 cell of the Keidel type. The accuracy of this method is, however, not very satisfactory. Calmè and Keyser[4] continuously titrate the iodine formed, with thiosulphate solution, in a special cell. Those methods which use gas chromatography in the final step, either for determination of carbon monoxide or of carbon dioxide, do not usually give such good values as Unterzaucher's original method.

The method which is described here is based on the continuous reduction of the iodine formed to iodide, at controlled potential.

Since iodine has been extensively studied in connection with coulometric measurements, and since with the help of modern electronic instrumentation quantities of electricity can be determined with very high accuracy, this procedure is very attractive.

Apparatus

The oxygen apparatus which is described here has been in use for about two years and is in principle the same as that of Unterzaucher up to and including the anhydroiodic acid tube. The iodine vapour which is formed here is led by the nitrogen gas stream (10 ml/min) through the electrically heated glass tube *A* (Fig. 1) down into the electrolysis cell *B*, also of glass, which contains 5 ml of 2*M* sodium iodide and 5 ml of 2*M* sodium perchlorate. To prevent the temperature from rising, the electrolysis cell is surrounded by a glass jacket through which cooling water is led in at *C* and out at *D*. *E* is a rotating platinum electrode consisting of a circular Pt gauze (36-mesh), diameter about 35 mm, fixed at one end to a rotating Teflon-coated shaft. The shaft rotates at about 400 rpm. *F* is a calomel reference electrode (Radiometer K 401). Electrolyte can be added to and removed from the cell through the hole stoppered by *G*. The nitrogen can leave the cell *via* a small hole in *G*. *H* is a circular Haldenwanger clay filter, diameter about 15 mm, fixed to the cell with special Haldenwanger cement. The anode, *K*, consists of a platinum gauze (36 mesh, 20 × 30 mm). The anode compartment contains 2*M* sodium perchlorate.

The platinum electrode, *E*, is connected *via* a mercury contact at the upper end of the rotating shaft with the positive input of an operational amplifier in a potentiostat of exactly the same construction as described by Karlsson and Karrman.[5] The reference electrode, *F*, is connected to the negative input of the operational amplifier, and the anode, *K*, to the output. The potential of the working electrode is always − 100 mV *vs.* the calomel electrode. The temperature of the tube *A* through which the iodine vapour is led from the anhydroiodic acid tube down to the working

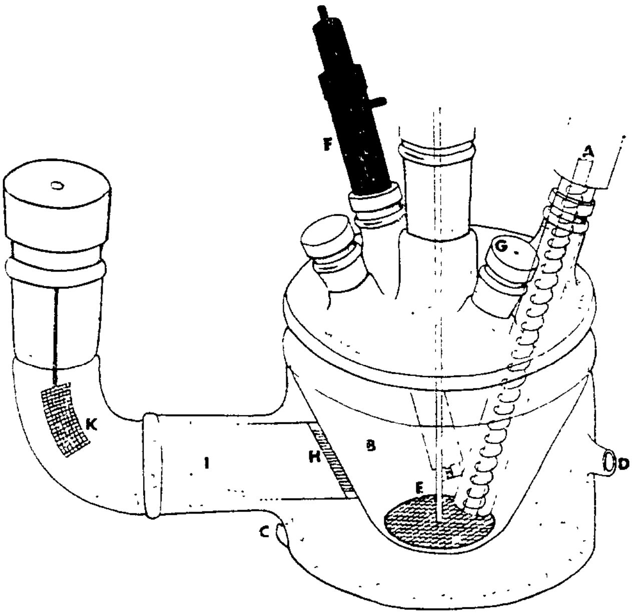


FIG. 1.—Electrolysis cell for oxygen determination.
A, double-walled electrically heated glass tube for transport of iodine vapour. *B*, cathode compartment with cooling jacket. *C* and *D*, inlet and outlet for cooling water. *E*, platinum cathode at the end of the rotating shaft. *F*, reference electrode. *G*, Teflon stopper with hole for release of nitrogen. *H*, Haldenwanger clay filter. *I*, anode compartment. *K*, anode, Pt-gauze.

electrode is about 120°. The quantity of electricity required to reduce the iodine is measured with an electronic integrator[5] and the value is read from a digital voltmeter (Solatron LM 1420·2).

Procedure

A 2–6 mg sample in a platinum boat is placed in the usual way in the pyrolysis tube. The cell is connected and a check made that the residual current is 15–20 μA before the movable furnace is put into position about 5 mm behind the boat. After about 3 min the current starts to increase rapidly and reaches a maximum value of 25–30 mA after 4–7 min. After about 13–14 min, depending on the nature of the sample, the residual current has again reached the 15–20 μA level, and the analysis is complete. The oxygen content is then calculated from the value U_0 read from the digital voltmeter, using the equation

$$\%\mathrm{O} = \frac{\mathrm{R}_1 \,.\, \mathrm{C} \,.\, (U_0 - U_\mathrm{B}) \,.\, 15 \,.\, 32}{R_2 \,.\, F \,.\, n \,.\, M \,.\, 6} \times 100 \qquad (1)$$

where R_1, R_2 and C are integrator components (see Fig. 2, Karlsson and Karrman[5]) and have in this case the values $R_1 = 0{\cdot}5\ \mathrm{M}\Omega$; $R_2 = 10\ \Omega$; $C = 10\ \mu\mathrm{F}$; $F = 96487$ C; $n = 2$ (number of electrons involved); M = weight of sample (mg); U_0 = integrator reading for sample (mV); U_B = integrator reading for blank (mV); 32 = molecular weight of oxygen.

The figures 15 and 6 come from the reaction between carbon monoxide and anhydroiodic acid. The electrical components have been accurately calibrated, and when the values are inserted in equation (1) the following simplified equation is obtained

$$\%\mathrm{O} = 0{\cdot}020718\,\frac{(U_0 - U_\mathrm{B})}{M} \qquad (2)$$

The integrator read-out for an analysis is 4000–5000 mV. The amount of sample is adjusted according to the oxygen content of the substance. The blank value in equation (1), U_B, is obtained by performing the analysis in the absence of the sample, and is 30 ± 3 mV. When the analysis is complete after 13–14 min (for certain substances which are more difficult to pyrolyse, a further

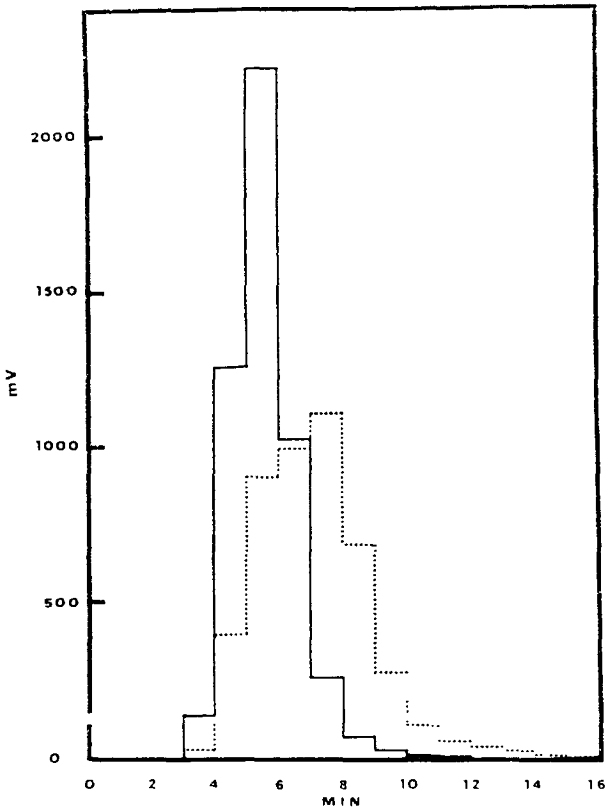


FIG. 2.—Histogram for the increase of the integrator read-out per unit time for the pyrolysis of benzoic acid (full line) and 3,5-dinitrobenzoic acid (dashed line).

1–2 min will be required) the residual current is 15–20 μA. This means that the residual current contributes about 2 mV/min to the integrator read-out.

RESULTS

The analyses can be carried out either by placing the movable furnace just behind the boat with the sample and then letting the furnace move over the boat, or by placing the furnace directly over the boat. With the latter procedure, the pyrolysis starts earlier and the total analysis time is reduced by 1–2 min. With the apparatus described here, the pyrolysis process can be followed continuously. Figure 2 shows 2 diagrams obtained by measuring the increase of the integrator read-out each whole minute, the time being counted from the moment the movable furnace was placed just behind the boat. It may be seen that benzoic acid is pyrolysed considerably faster than 3,5-dinitrobenzoic acid.

Table I gives the collected results from the determinations of oxygen on the milligram scale. It can be seen that the aromatic nitro-compounds give rise to a very small but significant systematic error. Some experiments have also been performed to determine the carbon dioxide and water evolved on heating calcium carbonate and barium chloride dihydrate (Table II). Thus when the amount of CO_2 is determined, only 2 of the 3 oxygen atoms in calcium carbonate are included in the calculated value. It has been shown previously, results not yet published, that the barium chloride contains 1·985 moles of H_2O which corresponds to an oxygen content of 13·02%; the measured value was 13·01%.

Table III shows some determinations made on the submilligram scale, where the weight of sample was 0·5–1·0 mg. The weighings were performed on a Rodder ultramicro torsion balance and a Sartorius electronic ultramicrobalance 4125. For these determinations, the diameters of the

TABLE I.—DETERMINATION OF OXYGEN ON SAMPLE WEIGHTS OF 2–6 mg

Substance	Calculated %O	Found %O ($\bar{x}$)	Number of determinations (n)	Standard deviation (s)	95% Confidence interval*
Benzoic acid	26·21	26·21	21	0·05	±0·023
Tris(hydroxymethyl)-aminomethane	39·62	39·61	20	0·09	±0·042
p-Chlorobenzoic acid	20·44	20·44	17	0·06	±0·031
m-Nitrobenzoic acid	38·30	38·20	20	0·11	±0·051
m-Dinitrobenzene	38·07	38·00	24	0·12	±0·051
3,5-Dinitrobenzoic acid	45·26	45·14	8	0·13	±0·109
1,4-Dimethoxybenzene	23·16	23·15	12	0·09	±0·057
Salicylic acid	34·75	34·74	5	0·04	±0·050
Urea	26·64	26·69	9	0·08	±0·061
8-Hydroxyquinoline	11·02	11·02	12	0·07	±0·044

* Calculated from $\bar{x} \pm \frac{s}{\sqrt{n}} \cdot t_{0.975(n-1)}$ from *Student's t*.

TABLE II

Substance	Calculated %O	Found %O	Number of determinations	Standard deviation	95% Confidence interval
Calcium carbonate	31·96	31·96	6	0·08	±0·084
Barium chloride dihydrate	13·02	13·01	9	0·04	±0·031

TABLE III.—DETERMINATION OF OXYGEN ON SAMPLE WEIGHTS OF 0·5–1·0 mg.

Substance	Calculated %O	Found %O	Number of determinations	Standard deviation	95% Confidence interval
Benzoic acid	26·21	26·23	8	0·08	±0·067
p-Chlorobenzoic acid	20·44	20·44	6	0·05	±0·052
Salicylic acid	34·75	34·68	6	0·10	±0·105
1,4-Dimethoxybenzene	23·16	23·11	5	0·13	±0·161
Tris(hydroxymethyl)-aminomethane	39·62	39·61	9	0·13	±0·100

pyrolysis tube and the anhydroiodic acid tube were decreased to half of the normal size, *i.e.*, the diameter of both tubes was about 5 mm and the amount of carbon and anhydroiodic acid was ¼ of the amount used in the normal apparatus. The nitrogen flow was 10 ml/min and the analysis time 11–12 min.

Acknowledgement—The authors thank Dr. Peter Sellers for correcting the English.

Department of Analytical Chemistry
University of Lund
P.O.B. 740, S-220 07 Lund 7, Sweden

K. J. KARRMAN
RONALD KARLSSON

Summary—An Unterzaucher apparatus for the determination of oxygen in organic compounds is used. The iodine vapour formed in the anhydroiodic acid tube is led by a stream of nitrogen to the cathodic chamber of an electrolysis cell. Here the iodine is reduced at controlled potential at a rotating Pt-electrode. The amount of electricity used is determined by an electronic integrator and read from a digital voltmeter. For weights of samples in the range 0·5–6 mg the standard deviation is about 0·08% oxygen.

Zusammenfassung—Zur Bestimmung von Sauerstoff in organischen Verbindungen wird ein Unterzaucher-Gerät verwendet. Der in der Röhre mit Anhydrojodsäure gebildete Joddampf wird mit einem Stickstoffstrom in die Kathodenkammer einer Elektrolysezelle überführt. Hier wird das Jod bei geregelter Spannung an einer rotierenden Pt-Elektrode reduziert. Die verbrauchte Elektrizitätsmenge wird durch einen elektronischen Integrator ermittelt und an einem Digitalvoltmeter abgelesen. Bei Probengewichten von 0,5–6 mg beträgt die Standardabweichung etwa 0,08% Sauerstoff.

Résumé—On utilise un appareil d'Unterzaucher pour le dosage de l'oxygène dans les composés organiques. La vapeur d'iode formée dans le tube à acide anhydroiodique est entrainée par un courant d'azote dans le compartiment cathodique d'une cellule à électrolyse. L'iode y est réduit à potentiel contrôlé sur une électrode tournante de platine. La quantité d'électricité utilisée est déterminée par un intégrateur électronique et lue sur un voltmètre digital. Pour des pesées d'échantillon comprises entre 0,5 et 6 mg, l'écart-type est d'environ 0,08% d'oxygène.

REFERENCES

1. J. Unterzaucher, *Analyst*, 1952, **77**, 584.
2. D. Fraisse and R. Levy, *Bull. Soc. Chim. France*, 1968, 445.
3. K.-I. Nakamura M.-A. Nishimura and T. Mitsui, *Microchem. J.*, 1970, **15**, 461.
4. P. Calmè and M. Keyser, *Microchim. Acta*, 1969, 1248.
5. R. Karlsson and K. J. Karrman, *Talanta*, 1971, **18**, 459.

Talanta, 1972, Vol. 19, pp. 71 to 74. Pergamon Press. Printed in Northern Ireland

Successive complexometric determination of thorium and uranium in sulphuric acid media

(*Received* 12 *April* 1971. *Accepted* 21 *August* 1971)

THE SUCCESSIVE complexometric determination of thorium(IV) and uranium(VI) in nitrate solution has been reported in the literature,[1] but a large quantity of sulphate or phosphate interferes seriously. The method, therefore, requires separation of thorium and uranium by precipitation with carbonate-free sodium hydroxide. Very large amounts of sulphate are present when sintered thorium oxides or thorium-uranium oxides are brought into solution by fusion with potassium bisulphate, and the precipitation procedure is quite time-consuming.

We have recently described the selective extraction determination of thorium[2,3] with *N*-butylaniline or *N*-benzylaniline in chloroform from sulphuric acid media. Gagliardi and Illmaier[4] have reported the specific extraction of uranium(VI) with the same reagents.

The present investigation, therefore, was undertaken to combine the extraction procedure with the successive complexometric determination of thorium and uranium.[1] It was found that extraction of uranium with *N*-butylaniline or *N*-benzylaniline in the presence of ascorbic acid and EDTA resulted in the removal of the interference of many cations such as zirconium, scandium, gallium, indium, yttrium, osmium, rhodium, ruthenium and thallium; palladium and platinum remained in the organic phase. The reduction of uranium(VI) with sodium dithionite for the titration of uranium (VI) was preferred as this reductant was found to be superior to ascorbic acid,[5] which reduces uranium (VI) in boiling solutions. The reduction of uranium(VI) with sodium dithionite at room temperature was rapid and quantitative. The de Heer method[1] was also modified, it having been found that a lower pH gave a sharper end-point.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-grade reagents. Aqueous solutions were prepared with doubly distilled water.

Zusammenfassung—Zur Bestimmung von Sauerstoff in organischen Verbindungen wird ein Unterzaucher-Gerät verwendet. Der in der Röhre mit Anhydrojodsäure gebildete Joddampf wird mit einem Stickstoffstrom in die Kathodenkammer einer Elektrolysezelle überführt. Hier wird das Jod bei geregelter Spannung an einer rotierenden Pt-Elektrode reduziert. Die verbrauchte Elektrizitätsmenge wird durch einen elektronischen Integrator ermittelt und an einem Digitalvoltmeter abgelesen. Bei Probengewichten von 0,5–6 mg beträgt die Standardabweichung etwa 0,08% Sauerstoff.

Résumé—On utilise un appareil d'Unterzaucher pour le dosage de l'oxygène dans les composés organiques. La vapeur d'iode formée dans le tube à acide anhydroiodique est entrainée par un courant d'azote dans le compartiment cathodique d'une cellule à électrolyse. L'iode y est réduit à potentiel contrôlé sur une électrode tournante de platine. La quantité d'électricité utilisée est déterminée par un intégrateur électronique et lue sur un voltmètre digital. Pour des pesées d'échantillon comprises entre 0,5 et 6 mg, l'écart-type est d'environ 0,08% d'oxygène.

REFERENCES

1. J. Unterzaucher, *Analyst*, 1952, **77**, 584.
2. D. Fraisse and R. Levy, *Bull. Soc. Chim. France*, 1968, 445.
3. K.-I. Nakamura M.-A. Nishimura and T. Mitsui, *Microchem. J.*, 1970, **15**, 461.
4. P. Calmè and M. Keyser, *Microchim. Acta*, 1969, 1248.
5. R. Karlsson and K. J. Karrman, *Talanta*, 1971, **18**, 459.

Talanta, 1972, Vol. 19, pp. 71 to 74. Pergamon Press. Printed in Northern Ireland

Successive complexometric determination of thorium and uranium in sulphuric acid media

(*Received* 12 *April* 1971. *Accepted* 21 *August* 1971)

THE SUCCESSIVE complexometric determination of thorium(IV) and uranium(VI) in nitrate solution has been reported in the literature,[1] but a large quantity of sulphate or phosphate interferes seriously. The method, therefore, requires separation of thorium and uranium by precipitation with carbonate-free sodium hydroxide. Very large amounts of sulphate are present when sintered thorium oxides or thorium-uranium oxides are brought into solution by fusion with potassium bisulphate, and the precipitation procedure is quite time-consuming.

We have recently described the selective extraction determination of thorium[2,3] with *N*-butylaniline or *N*-benzylaniline in chloroform from sulphuric acid media. Gagliardi and Illmaier[4] have reported the specific extraction of uranium(VI) with the same reagents.

The present investigation, therefore, was undertaken to combine the extraction procedure with the successive complexometric determination of thorium and uranium.[1] It was found that extraction of uranium with *N*-butylaniline or *N*-benzylaniline in the presence of ascorbic acid and EDTA resulted in the removal of the interference of many cations such as zirconium, scandium, gallium, indium, yttrium, osmium, rhodium, ruthenium and thallium; palladium and platinum remained in the organic phase. The reduction of uranium(VI) with sodium dithionite for the titration of uranium (VI) was preferred as this reductant was found to be superior to ascorbic acid,[5] which reduces uranium (VI) in boiling solutions. The reduction of uranium(VI) with sodium dithionite at room temperature was rapid and quantitative. The de Heer method[1] was also modified, it having been found that a lower pH gave a sharper end-point.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-grade reagents. Aqueous solutions were prepared with doubly distilled water.

TABLE I.—IONS WITHOUT EFFECT ON EXTRACTION OF URANIUM
[Uranium(VI) added, 5·952 mg, 2N H_2SO_4, 0·1M EDTA, N-butylaniline or N-benzylaniline in chloroform]

Foreign ion	Amount, *mg*	Foreign ion	Amount, *mg*
Hg(II)	100	Ni(II)	30
Ag(I)	100	Ca(II)	30
Pd(II)	20	Sr(II)	30
Au(III)	20	Mg(II)	30
Ru(III)	30	Mo(VI)	30
Ru(VII)*	30	V(III)	30
Os(VIII)*	30	V(V)*	30
Cu(II)	30	Ti(IV)*	25
Cd(II)	30	Sc(III)	25
Sb(III)	24	Tl(III)	40
Bi(III)	24	In(III)	30
Sn(II)	24	Y(III)	30
Fe(II)	30	Cr(III)	30
Al(III)	30	Fluoride†	20
Be(II)	30	Nitrate	100
Zr(IV)	27	Chloride	100
Ce(IV)*	30	Phosphate	100
Ce(III)	30	Citrate	100
Zn(II)	30	Tartrate	100
Mn(II)	30	Oxalate	100
Co(II)	30	EDTA	186

* Reduced with ascorbic acid.
† Masked with boric acid.

Thorium(IV) *solution*, 0·05M. Dissolve the required amount of thorium nitrate tetrahydrate in 0·001M nitric acid, and standardize against EDTA (Xylenol Orange indicator). Prepare more dilute solutions from it by accurate dilution.

Uranium(VI) *solution*, 0·05M. Dissolve the required amount of uranyl nitrate hexahydrate in 0·001M nitric acid and standardize gravimetrically with 8-hydroxyquinoline.

N-*butylaniline*. Dissolve 9·0 g of reagent (b.p. 241–242°) in 100 ml of chloroform.

N-*benzylaniline*. Dissolve 7·0 g of purified reagent[6] (m.p 36°, b.p. 180°/16 mbar) in 100 ml of chloroform.

Procedure

To an aliquot of solution containing up to a total of 45 mg of thorium(IV) and uranium(VI) in a 50-ml separatory funnel, add enough sulphuric acid and water to give 1–2·5N acid in the case of N-butylaniline and 3–4N acid in the case of N-benzylaniline, and a total volume of 10 ml. Add 15 ml of either N-butylaniline or N-benzylaniline solution in chloroform, shake the funnel vigorously for about 1 min and allow the layers to separate. Run off the organic layer into a 50-ml beaker. Extract again with 10 ml of the extractant solution. Strip thorium and uranium from the combined organic layers by shaking for 2 min with 30–40 ml of water. Transfer the aqueous layer to a 250-ml conical flask and dilute to about 100 ml. Adjust the pH to 2·5 ± 0·5 with 2M ammonia solution (narrow-range pH paper or pH-meter). Add 8 drops of 0·1% Xylenol Orange solution and titrate with 0·01M EDTA (yellow end-point). Then add roughly 100% excess of EDTA with respect to uranium. Add sodium dithionite till the brown colour of the solution changes to green. Then add *ca.* 10 drops of 37% formaldehyde solution, followed by 8 drops of Xylenol Orange solution. Adjust the pH to 2·5 ± 0·5 and titrate with standard thorium solution (red end-point).

RESULTS AND DISCUSSION

Both thorium(IV) and uranium(VI) can be selectively and quantitatively extracted from sulphuric acid media. The extraction of uranium(VI) in the presence of ascorbic acid and sufficient 0·1M EDTA obviates the interference of most cations[2,3] and improves the selectivity of the Gagliardi method[4] (Table I). Excess of ascorbic acid does not interfere. Palladium(II) and platinum(II) or (IV) remain in the organic phase. Nitrate, chloride, borate, arsenate, citrate and tartrate do not interfere. Phosphate and oxalate, which interfere in most methods for the extraction of thorium and

TABLE II.—ANALYSIS OF BINARY MIXTURES OF THORIUM AND URANIUM

Added		Th(IV) found, *mg*	Error, %	Uranium(VI) found, *mg*	Error, %
Th(IV), *mg*	U(VI), *mg*				
5·78	2·38	5·78	0·0	2·35	−1·3
11·56	7·14	11·62	+0·5	7·10	−0·6
17·34	11·90	17·30	−0·2	11·96	+0·5
17·34	23·80	17·40	+0·4	23·70	−0·4
2·32	5·78	2·31	−0·4	5·81	+0·5
5·78	30·94	5·81	−0·5	30·76	−0·6
11·56	11·90	11·62	+0·5	11·84	−0·5

uranium, do not interfere. Fluoride interferes seriously but can easily be masked with boric acid in dilute sulphuric acid.

Typical results obtained for mixtures are summarized in Table II. It was found that 25 ml of *N*-butylaniline or *N*-benzylaniline are sufficient to extract a total of 48 mg of thorium and uranium. Larger amounts can be extracted with an increased amount of extractant. None of the experimental conditions is critical. The method is simple, rapid, accurate and selective.

M. M. L. KHOSLA

Defence Laboratory
Jodhpur, India

S. P. RAO

Department of Chemistry
University of Jodhpur
Jodhpur, India

Summary—A selective analytical extraction method for rapid successive complexometric determination of thorium(IV) and uranium(VI) in sulphuric acid media is described. The method is based on the extraction of thorium and uranium from sulphuric acid media with *N*-butylaniline or *N*-benzylaniline in chloroform. Both thorium and uranium are selectively and quantitatively extracted in the presence of ascorbic acid and EDTA. Most cations and anions do not interfere. The reduction of uranium(VI) with sodium dithionite at room temperature is rapid and quantitative and superior to that with ascorbic acid, which reduces uranium(VI) in boiling solution. The method is simple, rapid and accurate, and the experimental conditions are not highly critical.

Zusammenfassung—Eine selektive analytische Extraktionsmethode zur raschen komplexometrischen Bestimmung von Thorium(IV) und Uran(IV) nacheinander in schwefelsaurer Lösung wird beschrieben. Die Methode beruht auf der Extraktion von Thoruim und Uran aus schwefelsaurer Lösung mit N-Butylanilin oder N-Benzylanilin in Chloroform. In Gegenwart von Ascorbinsäure und EDTA werden sowohl Thorium als auch Uran selektiv und quantitativ extrahiert. Die meisten Kationen und Anionen stören nicht. Die Reduktion von Uran(VI) mit Natriumdithionit bei Zimmertemperatur verläuft rasch und quantitativ und ist der Reduktion mit Ascorbinsäure überlegen, die Urban(VI) in siedender Lösung reduziert. Die Methode ist einfach, schnell und genau; die Versuchsbedingungen müssen nicht sehr kritisch eingehalten werden.

Résumé—On décrit une méthode d'extraction analytique sélective pour la détermination complexométrique successive rapide du thorium(IV) et de l'uranium(IV) en milieux acide sulfurique. La méthode est basée sur l'extraction du thorium et de l'uranium des milieux acide sulfurique par la N-butylaniline ou la N-benzylaniline en chloroforme. Le thorium et l'uranium sont tous deux sélectivement et quantitativement

extraits en la présence d'acide ascorbique et d'EDTA. La plupart des cations et des anions ne gênent pas. La réduction de l'uranium(IV) par le dithionite de sodium à température ordinaire est rapide et quantitative et supérieure à celle obtenue avec l'acide ascorbique, qui réduit l'uranium(IV) en solution bouillante. La méthode est simple, rapide et précise, et les conditions experimentales ne sont pas extrémement essentielles.

REFERENCES

1. B. H. J. de Heer, T. van der Plas and M. E. A. Hermans, *Anal. Chim. Acta*, 1965, **32**, 292.
2. M. M. L. Khosla and S. P. Rao, *Microchem. J.*, in the press.
3. *Idem*, *Anal. Chim. Acta*, in the press.
4. E. Gagliardi and B. Illmaier, *Mikrochim. Acta*, 1968, 1259.
5. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 82.
6. H. Gilman and A. H. Balatt, *Organic Syntheses*, *Coll. Vol. I*, 2nd Ed., p. 103. Wiley, New York, 1958.

Talanta, 1972, Vol. 19, pp. 74 to 76. Pergamon Press. Printed in Northern Ireland

Titrimetric determination of arsenic(III) with potassium dichromate, using redox indicators

(*Received* 16 *April* 1971. *Accepted* 20 *August* 1971)

THE DETERMINATION of arsenic(III) is of importance in the assay of pharmaceuticals, insecticides, glasses, and alloys. Also, several oxidizing agents are estimated indirectly by treatment with excess of arsenite and back-titration of the excess with a suitable oxidant. Thus de Bacho[1] determined permanganate, manganese dioxide, barium peroxide, chlorate, hypochlorite, persulphate *etc.* and Schreyer *et al.*[2] determined potassium ferrate. Willard and Young[3] standardized dichromate solutions similarly, titrating the surplus arsenite with cerium(IV) sulphate, with osmium tetroxide as catalyst and ferroin as indicator. Van der Meulen[4] precipitated lead as chromate with a measured and excessive amount of dichromate solution and estimated the excess by reducing with excess of arsenite and back-titrating with bromate.

Arsenic(III) has been titrated with potassium permanganate, potassium iodate, iodine monochloride, iodine, potassium bromate, chloramine-T, sodium chlorite, sodium hypochlorite, potassium periodate, cerium(IV) sulphate and other oxidizing agents, most of which have disadvantages, such as unavailability in analytical grade purity, instability in solution or high cost. Potassium dichromate is unique in that it is free from these drawbacks, but has not previously been used successfully for titration of arsenic(III). (Pound[5] obtained high results, using diphenylamine as indicator.) We have now made an investigation of the use of potassium dichromate for determination of arsenic(III) and established conditions for accurate titrations using ferroin and *N*-phenylanthranilic acid as indicators.

EXPERIMENTAL

Solutions

Sodium arsenite solution, 0·1*N*. Prepared from arsenious oxide dried at 105–110° for 1 hr and stored in a Pyrex bottle kept in the dark. The solution was made acidic to avoid oxidation by atmospheric oxygen. Demineralized water was used for preparing the solution because traces of heavy metal ions are known to catalyse the oxidation.

Potassium dichromate solution, 0·1*N*. Stored in Pyrex.

All chemicals used were of analytical reagent quality.

Titration of arsenic(III)

In a preliminary study by photometric titration the rate of oxidation of arsenite by dichromate was found to increase with increasing acid concentration, becoming very fast in > 6*N* sulphuric acid. Oxidation of ferroin becomes fast enough in 7·5–8·5*N* sulphuric acid, but reduction of ferriin by extraits en la présence d'acide ascorbique et d'EDTA. La plupart des cations et des anions ne gênent pas. La réduction de l'uranium(IV) par le dithionite de sodium à température ordinaire est rapide et quantitative et supérieure à celle obtenue avec l'acide ascorbique, qui réduit l'uranium(IV) en solution bouillante. La méthode est simple, rapide et précise, et les conditions experimentales ne sont pas extrémement essentielles.

REFERENCES

1. B. H. J. de Heer, T. van der Plas and M. E. A. Hermans, *Anal. Chim. Acta*, 1965, **32**, 292.
2. M. M. L. Khosla and S. P. Rao, *Microchem. J.*, in the press.
3. *Idem*, *Anal. Chim. Acta*, in the press.
4. E. Gagliardi and B. Illmaier, *Mikrochim. Acta*, 1968, 1259.
5. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, 1957, **46**, 82.
6. H. Gilman and A. H. Balatt, *Organic Syntheses*, *Coll. Vol. I*, 2nd Ed., p. 103. Wiley, New York, 1958.

Talanta, 1972, Vol. 19, pp. 74 to 76. Pergamon Press. Printed in Northern Ireland

Titrimetric determination of arsenic(III) with potassium dichromate, using redox indicators

(*Received* 16 *April* 1971. *Accepted* 20 *August* 1971)

THE DETERMINATION of arsenic(III) is of importance in the assay of pharmaceuticals, insecticides, glasses, and alloys. Also, several oxidizing agents are estimated indirectly by treatment with excess of arsenite and back-titration of the excess with a suitable oxidant. Thus de Bacho[1] determined permanganate, manganese dioxide, barium peroxide, chlorate, hypochlorite, persulphate *etc.* and Schreyer *et al.*[2] determined potassium ferrate. Willard and Young[3] standardized dichromate solutions similarly, titrating the surplus arsenite with cerium(IV) sulphate, with osmium tetroxide as catalyst and ferroin as indicator. Van der Meulen[4] precipitated lead as chromate with a measured and excessive amount of dichromate solution and estimated the excess by reducing with excess of arsenite and back-titrating with bromate.

Arsenic(III) has been titrated with potassium permanganate, potassium iodate, iodine monochloride, iodine, potassium bromate, chloramine-T, sodium chlorite, sodium hypochlorite, potassium periodate, cerium(IV) sulphate and other oxidizing agents, most of which have disadvantages, such as unavailability in analytical grade purity, instability in solution or high cost. Potassium dichromate is unique in that it is free from these drawbacks, but has not previously been used successfully for titration of arsenic(III). (Pound[5] obtained high results, using diphenylamine as indicator.) We have now made an investigation of the use of potassium dichromate for determination of arsenic(III) and established conditions for accurate titrations using ferroin and *N*-phenylanthranilic acid as indicators.

EXPERIMENTAL

Solutions

Sodium arsenite solution, 0·1*N*. Prepared from arsenious oxide dried at 105–110° for 1 hr and stored in a Pyrex bottle kept in the dark. The solution was made acidic to avoid oxidation by atmospheric oxygen. Demineralized water was used for preparing the solution because traces of heavy metal ions are known to catalyse the oxidation.

Potassium dichromate solution, 0·1*N*. Stored in Pyrex.

All chemicals used were of analytical reagent quality.

Titration of arsenic(III)

In a preliminary study by photometric titration the rate of oxidation of arsenite by dichromate was found to increase with increasing acid concentration, becoming very fast in > 6*N* sulphuric acid. Oxidation of ferroin becomes fast enough in 7·5–8·5*N* sulphuric acid, but reduction of ferriin by

TABLE I.—TITRATION OF ARSENIC(III) AT ROOM TEMPERATURE WITH POTASSIUM DICHROMATE

Medium	Arsenic(III), *meq* Taken	Arsenic(III), *meq* Found	Relative error, %
8*N* H_2SO_4	0·9000	0·9000	0·0
+	0·7980	0·8000	+0·3
1 ml of 0·005*M* KI	0·7000	0·7020	+0·3
ferroin indicator	0·6000	0·5980	−0·4
	0·5000	0·5000	0·0
	0·4000	0·4000	0·0
	0·3228	0·3232	+0·1
	0·3228	0·3232	+0·1
	0·2178	0·2180	+0·1
8*N* H_2SO_4	0·8980	0·8980	0·0
+	0·8020	0·8000	−0·3
0·5 ml of 0·005*M* ICl	0·6000	0·6000	0·0
ferroin indicator	0·5260	0·5240	+0·4
	0·4060	0·4070	+0·2
	0·3280	0·3270	−0·3
10*N* H_2SO_4	0·9020	0·9020	0·0
+	0·8000	0·8000	0·0
1 ml of 0·005*N* KI	0·7020	0·7020	0·0
N-phenylanthranilic	0·6140	0·6140	0·0
acid indicator	0·5020	0·5010	−0·2
	0·4200	0·4200	0·0
	0·3160	0·3150	−0·3
	0·2160	0·2150	−0·5

arsenic(III) is then slow. To make this second reaction fast it was found necessary to add a catalyst, 0·05 ml of 0·1*M* potassium iodide for 50 ml of titration mixture. As iodide will be oxidized to iodine by potassium dichromate at the end of the titration, a suitable correction has to be made for it. Similar observations were made when *N*-phenylanthranilic acid was used as indicator, except that a wider range of acid concentration (8–11*N*) can be used.

Procedure

Dilute the arsenic(III) solution to about 30 ml, then add slowly and with stirring enough sulphuric acid (1+1) to make the mixture 7·5–8·5*N* in acid when diluted to 50 ml. Cool to room temperature, add 1 ml of 0·005*M* potassium iodide and 0·05 ml of 0·025*M* ferroin and dilute to 50 ml and titrate with dichromate, rapidly until within 0·2 ml of the end-point, then dropwise with a wait of 30–40 sec between drops; use a magnetic stirrer. The end point is indicated by the sharp change in colour from brown to blue-grey. If more catalyst is used, a brown turbidity appears, which is very likely due to an insoluble ferroin–iodine complex. Deduct 0·06 ml of 0·1*N* dichromate to allow for oxidation of the catalyst and indicator. Alternatively, adjust the acidity to 8–10*N* and use 2 drops of 0·2% *N*-phenylanthranilic acid solution as indicator.

RESULTS AND DISCUSSION

The reactions underlying the titration may be postulated a follows:

$$\text{ferroin} + \text{Cr(VI)} \xrightarrow{>7{\cdot}5N\ H_2SO} \text{ferriin} + \text{Cr(V)},\ \text{fast}$$

$$\text{Cr(V)} + \text{As(III)} \longrightarrow \text{Cr(III)} + \text{As(V)},\ \text{fast}$$

$$\text{ferriin} + \text{As(III)} \xrightarrow{7{\cdot}5N\ H_2SO_4} \text{ferroin} + \text{As(IV)},\ \text{slow}$$

$$\text{ferriin} + \text{I}^- \text{———} \text{I}^0 + \text{ferroin},\ \text{fast}$$

$$\text{I}^0 + \text{As(III)} \text{———} \text{As(IV)} + \text{I}^-,\ \text{fast}$$

$$\text{As(IV)} + \text{Cr(VI)} \text{———} \text{Cr(V)} + \text{As(V)},\ \text{fast}$$

$$\text{or As(IV)} + \text{ferriin} \text{———} \text{As(V)} + \text{ferroin},\ \text{fast}$$

We have also used 0·5 ml of 0·005*M* iodine monochloride as catalyst, and then the volume of dichromate solution consumed was about 0·05 ml less than the theoretical on account of the oxidizing action of iodine monochloride on arsenic(III). Some representative results are presented in Table I, with the corrections applied.

Interferences

Iron(III) (0·2–2·0 meq), chromium(III) (0·2–2·0 meq), aluminium(III) (0·2–2·0 meq) and manganese(II) (0·5–2·0 meq) do not interfere. Iron(II) and similar reductants interfere by reacting with the potassium dichromate.

G. Gopala Rao
B. Sarojini
Muralikrishna Gandikota

Department of Chemistry
Andhra University
Waltair, India

Summary—Experimental conditions have been established for the accurate direct titrimetric determination of arsenic(III) with potassium dichromate, using ferroin and *N*-phenylanthranilic acid as redox indicators. Interferences have been considered.

Zusammenfassung—Die Versuchsbedingungen für die genaue direkte titrimetrische Bestimmung von Arsen(III) mit Kaliumdichromat und Ferroin oder *N*-Phenylanthranilsäure als Redoxindikatoren wurden ermittelt. Störungen werden erörtert.

Résumé—On a établi les conditions expérimentales pour le dosage titrimétrique direct précis de l'arsenic(III) avec le bichromate de potassium, en utilisant la ferroïne et l'acide N-phénylanthranilique comme indicateurs redox. On a considéré les interférences.

REFERENCES

1. F. de Bacho, *Ann. Chim. Appl.*, 1919, **12**, 153.
2. J. M. Schreyer, G. W. Thompson and L. T. Ockerman, *Anal. Chem.*, 1950, **22**, 691.
3. H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 57.
4. J. H. van der Meulen, *Chem. Weekblad*, 1926, **45**, 653.
5. J. R. Pound, *Chem. Eng. Mining. Rev.*, 1945, **38**, 87.

Talanta, 1972, Vol. 19, pp. 76 to 80. Pergamon Press. Printed in Northern Ireland

The use of triethanolamine in a buffer for the determination of fluoride in calcium and transition metal orthophosphates, using a fluoride-selective electrode

(*Received* 26 *March*. *Accepted* 3 *July* 1971)

The use of a fluoride-selective electrode[1,2] has largely superseded, at least for inorganic analysis, the earlier spectrophotometric methods[3–8] for the determination of traces of fluoride. Whilst the fluoride electrode "senses" only ionic fluoride below pH 8, it is sensitive to hydroxide ions at higher pH values. In addition, the presence of undissociated hydrofluoric acid, or HF_2^- ions, (which can exist below about pH 3·5) results in an apparent loss of fluoride ions as sensed by the electrode. Further, the formation of complexes with metal cations reduces the concentration of free, ionic fluoride in the system. The electrode potential is also affected by changes in the ionic strength of the solution, which are often overcome by the addition of a buffer of high ionic strength, such that the variation in the ionic strength of the sample solution will have but a small effect on that of the buffered system. An early example of this type of buffer for fluoride determination is "Total Ionic Strength Adjustment Buffer"[9] (TISAB). Recently, criticisms have been advanced against the use of this buffer in calcium orthophosphate systems[10–12] on the grounds that the acetate ion forms an insoluble calcium complex. The use of the citrate ion, usually added as the trisodium salt, as a buffer in place of TISAB appears to overcome this objection. In a recent communication[11] we described a method utilizing hydrochloric acid to dissolve solid calcium orthophosphates, and trisodium citrate for pH control. Whilst this method has proved useful for the analysis of pure calcium orthophosphates, and has also been used with success on many other bivalent metal orthophosphates, it has been found

We have also used 0·5 ml of $0{\cdot}005M$ iodine monochloride as catalyst, and then the volume of dichromate solution consumed was about 0·05 ml less than the theoretical on account of the oxidizing action of iodine monochloride on arsenic(III). Some representative results are presented in Table I, with the corrections applied.

Interferences

Iron(III) (0·2–2·0 meq), chromium(III) (0·2–2·0 meq), aluminium(III) (0·2–2·0 meq) and manganese(II) (0·5–2·0 meq) do not interfere. Iron(II) and similar reductants interfere by reacting with the potassium dichromate.

G. Gopala Rao
B. Sarojini
Muralikrishna Gandikota

Department of Chemistry
Andhra University
Waltair, India

Summary—Experimental conditions have been established for the accurate direct titrimetric determination of arsenic(III) with potassium dichromate, using ferroin and *N*-phenylanthranilic acid as redox indicators. Interferences have been considered.

Zusammenfassung—Die Versuchsbedingungen für die genaue direkte titrimetrische Bestimmung von Arsen(III) mit Kaliumdichromat und Ferroin oder *N*-Phenylanthranilsäure als Redoxindikatoren wurden ermittelt. Störungen werden erörtert.

Résumé—On a établi les conditions expérimentales pour le dosage titrimétrique direct précis de l'arsenic(III) avec le bichromate de potassium, en utilisant la ferroïne et l'acide N-phénylanthranilique comme indicateurs redox. On a considéré les interférences.

REFERENCES

1. F. de Bacho, *Ann. Chim. Appl.*, 1919, **12**, 153.
2. J. M. Schreyer, G. W. Thompson and L. T. Ockerman, *Anal. Chem.*, 1950, **22**, 691.
3. H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 57.
4. J. H. van der Meulen, *Chem. Weekblad*, 1926, **45**, 653.
5. J. R. Pound, *Chem. Eng. Mining. Rev.*, 1945, **38**, 87.

Talanta, 1972, Vol. 19, pp. 76 to 80. Pergamon Press. Printed in Northern Ireland

The use of triethanolamine in a buffer for the determination of fluoride in calcium and transition metal orthophosphates, using a fluoride-selective electrode

(*Received* 26 *March. Accepted* 3 *July* 1971)

The use of a fluoride-selective electrode[1,2] has largely superseded, at least for inorganic analysis, the earlier spectrophotometric methods[3–8] for the determination of traces of fluoride. Whilst the fluoride electrode "senses" only ionic fluoride below pH 8, it is sensitive to hydroxide ions at higher pH values. In addition, the presence of undissociated hydrofluoric acid, or HF_2^- ions, (which can exist below about pH 3·5) results in an apparent loss of fluoride ions as sensed by the electrode. Further, the formation of complexes with metal cations reduces the concentration of free, ionic fluoride in the system. The electrode potential is also affected by changes in the ionic strength of the solution, which are often overcome by the addition of a buffer of high ionic strength, such that the variation in the ionic strength of the sample solution will have but a small effect on that of the buffered system. An early example of this type of buffer for fluoride determination is "Total Ionic Strength Adjustment Buffer"[9] (TISAB). Recently, criticisms have been advanced against the use of this buffer in calcium orthophosphate systems[10–12] on the grounds that the acetate ion forms an insoluble calcium complex. The use of the citrate ion, usually added as the trisodium salt, as a buffer in place of TISAB appears to overcome this objection. In a recent communication[11] we described a method utilizing hydrochloric acid to dissolve solid calcium orthophosphates, and trisodium citrate for pH control. Whilst this method has proved useful for the analysis of pure calcium orthophosphates, and has also been used with success on many other bivalent metal orthophosphates, it has been found that certain metal ions are complexed preferentially with fluoride rather than with citrate under the conditions used in the determination, and therefore give rise to low readings for fluoride content of the solutions when this is determined electrometrically. Because many mineralogical and biological samples of calcium orthophosphates contain appreciable quantities of some of these ions, we have developed a method of minimizing the interference from them in fluoride determinations by employing triethanolamine in the presence of citric acid as the complexing ligands, at a pH in the range 4·5–7·5.

EXPERIMENTAL

Reagents

Dissolution acid—either *A* or *B*. *A*: 2*M* in each of hydrochloric and citric acids: 420 g of analytical-reagent grade citric acid dissolved in 700 ml of demineralized distilled water and 172·5 ml of analytical-reagent grade concentrated hydrochloric acid and diluted to 1 litre with demineralized distilled water. *B*: 2*M* in each of perchloric and citric acids: 166 ml of analytical-reagent grade perchloric acid (70–72%) in place of the hydrochloric acid in *A*.

Triethanolamine (*TEA*) *solution*. Reagent-grade TEA (266 ml) diluted to 1 litre with demineralized distilled water.

Instruments

For pH. Pye 290 pH meter with a Pye-Ingold E-07 combination pH electrode.

For pF. Orion 94-09 or 94-09A fluoride-selective electrode with a Cambridge Instrument 42528 ceramic plug calomel reference electrode, or a Radiometer K401 calomel reference electrode.

Radiometer mains-operated PHM 53 selective-ion meter.

Procedure

Between 0·2 and 0·3 g of solid calcium orthophosphate (or other orthophosphate) is dissolved in 5 ml of the dissolution acid, then 5 ml of demineralized distilled water are added followed by 15 ml of TEA. (The quantities may be scaled down or up as appropriate) The pH of the system should now be in the range 5·0–5·8. The pF is now measured after allowing sufficient time for the electrode to equilibrate. (N.B. A minor modification introduced after this procedure was developed, a Radiometer PHM 51 meter, which has a recorder output, may be connected to a suitable pen recorder to facilitate the taking of readings when the response time is long (this is only necessary when the fluoride content of the system is less than $5 \times 10^{-5}M$).) The PHM 51 is a combined pH and univalent-ion meter; whilst for many purposes it is as good as the PHM 53 for selective ion work, experience of both meters in these laboratories suggests that the PHM 53 meter, despite its longer response time, yields more reproducible results with fluoride-selective electrodes than does the PHM 51. The fluoride content of the solution may be determined by reference to a suitable calibration curve constructed by substitution of 5 ml of an appropriate standard fluoride solution (analytical-reagent grade sodium fluoride) for the 5 ml of demineralized distilled water. The calibration curve method also affords a method for the determination of fluoride in aqueous solutions. Higher pH up to 7·5 may be used if desired simply by increasing the amount of TEA used. Some decrease in the sensitivity occurs at pH higher than 6·0.

DISCUSSION

The technique described here differs from that developed earlier in these laboratories in that citric acid is substituted for trisodium citrate, and triethanolamine is used to buffer the system at the desired pH. A 2*M* solution of TEA has a pH of *ca* 9·2. The total ionic strength of the final solution is about 1·7–1·9, which is quite usual for fluoride determination. It is, however, unusual to carry out the determination at a pH much above 6·0 because interference from hydroxide ions is then more likely. We explored the extent of hydroxide interference in the system described here, by using 2*M* TEA solutions, and reducing the quantity of dissolution acid used, the total volume being kept constant by addition of demineralized distilled water. This had the effect of increasing the pH without greatly decreasing the ionic strength. Two standard fluoride solutions were used for these determinations: 5×10^{-3} and $10^{-4}M$. Hydroxide ion interference occurred in both cases when the pH exceeded 8·2. Thus in the range pH 5·0–7·5 which may be used in this work, no hydroxide ion interference should occur. However, if an alkaline solid sample or solution is being analysed it may be advisable to ascertain the pH of the sample solution before the fluoride determination is made and, if necessary, to reduce the pH to below 7·5. The optimum pH for the determination is pH 5·4.

Many transition metal ions form soluble complexes of the type MF_x^{x-y} (where x is the number of fluoride ions in the complex, and y is the charge on the metal cation M). Until recently, little was known of the nature of metal-ion interactions with fluoride ions. With the advent of the fluoride-selective electrode, more knowledge has been gained of these systems. Recently, the stability constants of fluoride complexes of H^{+},[13] Al(III) and Fe(III),[14] Sn(II)[15] and Cd, Mg, Ni, and Ag(II)[16] have been determined. Whilst bivalent transition metal fluoride complexes are relatively weak, they are nevertheless significant in that distinctly low values for fluoride are recorded in the presence of these metal ions. That these complexes are not entirely dissociated by hydrochloric acid–citric acid buffer at pH 4·8–5·5 is shown in Table I.

It has been shown recently[17] that TEA will form complexes with a number of bivalent transition metal ions, and under certain conditions, these can be obtained as solid compounds. We suggest that some complexing of these ions by TEA is occurring in aqueous solution, and that this, together with the higher pH used in this work for fluoride determination, results in a more complete recovery of the fluoride present (see Table I).

TABLE I.—DETERMINATION OF FLUORIDE IN THE PRESENCE OF VARIOUS METAL IONS WITH USE OF HYDROCHLORIC ACID–CITRATE OF PERCHLORIC ACID–CITRIC ACID–TEA BUFFERS

Metal ion (25 ppm)	Fluoride found, *ppm*			
	Hydrochloric acid–citrate buffer		Perchloric acid–citric acid–TEA, pH 7	
	A*	B†	A*	B†
None	48·5	4·9	48·5	4·92
Fe(II)	44·2	4·2	48·4	4·90
Zn	48·0	4·8	48·5	4·91
Ni	48·4	4·9	48·6	4·90
Co(II)	48·2	4·85	48·5	4·95
Mn(II)	47·5	4·8	48·5	4·95
Cr(III)	47·0	4·42	48·4	4·89
Cu(II)	46·5	4·5	48·4	4·89
Al (as SO_4^{2-})	10·7	0·0	15·5	0·0

* 47·5 ppm fluoride taken.

† 4·75 ppm fluoride taken.

Solutions prepared from 1 ml of 500-ppm metal ion solution + 10 ml of 100-ppm or 10-ppm sodium fluoride solution + 10 ml of buffer solution.

Of the ions investigated, only aluminium causes incomplete recovery of fluoride. This is not altogether surprising as the AlF_6^{3-} ion is one of the most stable complex ions known. With this proviso, the method described here appears to overcome the majority of the interferences in the electrometric determination of fluoride that arise from complexing with metal ions. Repeated determinations on samples gave a reproducibility of better than ±3%, similar to that obtained by our earlier method. There was no significant difference in the results obtained by using perchloric rather than hydrochloric acid for sample dissolution. Neither perchlorate nor chloride interfered when present in 5000-fold amounts nor calcium nor orthophosphate (as HPO_4^{2-} or $H_2PO_4^{-}$) when present in 3000-fold amounts. The method has also been used for the determination of fluoride in samples of transition metal orthophosphates (Table II).

A comparison was made to determine the lower limit of fluoride determination by this method and by our earlier method. A calibration curve was constructed for both methods, using freshly prepared solutions of sodium fluoride (analytical-reagent grade) of concentrations in the range 10^{-1}–$10^{-8}M$. The method described here gave a reproducible linear calibration curve to 7 × $10^{-5}M$, 1·7 × $10^{-5}M$, after which there was a gradual but reproducible curvature to 8 × $10^{-7}M$. At fluoride at pH 7·0 and circa 10^{-6} M at pH 5·4 after which it curved off sharply. The curve obtained by using our earlier method[11] was linear to concentrations below this, the curve fell away sharply. It would appear therefore, that this present method is not readily applicable for the determination of fluoride at concentrations much below $10^{-4}M$ at the higher pH which may be used, whereas our previous method may, and has been, used successfully down to $10^{-6}M$. (N.B. These concentrations represent the concentration of fluoride in the buffered solutions and not in the sample solution. At these very low concentrations, a response time of 30 min is required in order to obtain reproducible results.)

TABLE II.—DETERMINATION OF FLUORIDE IN VARIOUS METAL ORTHOPHOSPHATES

Compound	Fluoride found, *ppm*				
	In sample	With 10 *ppm* added fluoride	Relative std. devn., %	With 1000 *ppm* added fluoride	Relative std. devn., %
Cupric apatite	495	504	1	1502	3
Nickel orthophosphate	1064	—	—	2050	2
Cobalt orthophosphate	238	248	1	1241	1
$CuHPO_4$	8·2	17·9	1	1009	1
$Zn_3(PO_4)_2{\cdot}4H_2O$	3·7	13·6	1	1001	1
$Ni_3(PO_4)_2 7H_2O$	19·5	29·4	1	1021	1
$CaHPO_4$	8·2	19·0	1	1009	1
$CaHPO_4{\cdot}2H_2O$	20·2	30·1	1	1021	1
$Ca_5OH(PO_4)_3$*	58·2	68·3	1	1054	1
$Ca_5F(PO_4)_3$†	37·8 × 10^3	—	—	38·8 × 10^3	2

* Prepared by reaction from $CaHPO_4{\cdot}2H_2O$ in 0·1*M* sodium hydroxide solution.[18]
† Prepared by reaction from $CaHPO_4{\cdot}2H_2O$ in 0·1*M* sodium fluoride solution.[19]

Care of the electrodes

The sensitivity and response time of the fluoride-selective electrode appear to be directly related to the treatment received by the electrode immediately before the determination. It was found that optimum sensitivity and response could be obtained by storage of the electrode in a buffer solution made $10^{-3}M$ in sodium fluoride. Care should be taken that this solution does not evaporate, as it has been found that a solution more than 10*M* in TEA may damage the electrode. Immediately before use, and immediately after, the electrode should be washed with demineralized distilled water, and carefully dried with a tissue, after which the electrode is ready for use. Alternatively, the electrode may be stored in demineralized distilled water. It should be noted that although the Cambridge Instrument type 42528 calomel reference electrode appeared to survive storage under either of these conditions satisfactorily, the Radiometer type K401 calomel electrode suffered diffusion of KCl from the electrode to the storage solution. This electrode should therefore be stored dry. Repeated swings from low a_{F^-} samples to high a_{F^-} samples should be avoided, and if several samples are to be analysed which contain different fluoride levels, it is advisable to begin with those at the lower levels. Little difference was found between the sensitivity of the older Orion 94-09 fluoride-selective electrode, which has been used in these laboratories continuously for over 4 years, and a new example of the newer type of electrode, Orion 94-09A.

Acknowledgement—This work was supported in part by Colgate-Palmolive Ltd.

EDWARD J. DUFF
J. L. STUART

Department of Preventive Dentistry
Turner Dental School
The University
Manchester, U.K.

Summary—A method is described for the determination of fluoride in inorganic orthophosphates. Interference by complex-forming metal ions is avoided by the use of a citric acid–triethanolamine buffer, pH < 7·5.

Zusammenfassung—Ein Verfahren zur Bestimmung von Fluorid in anorganischen Orthophosphaten wird beschrieben. Eine Störung durch komplexbildende Metallion wird durch Verwendung eines Puffers aus Zitronensäure und Triäthanolamin bei pH < 7,5 vermieden.

Résumé—On décrit une méthode pour le dosage du fluorure dans les orthophosphates minéraux. On évite l'interférence des ions métalliques formant des complexes par l'emploi d'un tampon acide citrique-triéthanolamine, pH < 7,5.

REFERENCES

1. M. S. Frant and J. W. Ross, *Science*, 1966, **154**, 1553.
2. see *Ion Selective Electrodes*, ed. R. A. Durst, *Natl. Bur. Stds. Monograph* 314, 1969.
3. H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 784.
4. H. W. Wharton, *Anal. Chem.*, 1962, **34**, 296.
5. S. A. Leach and W. D. Armstrong, *Arch. Oral Biol.*, 1963, **8**, 81.
6. L. Singer and W. D. Armstrong, *Anal. Chem.*, 1959, **31**, 105.
7. R. J. Hall, *Analyst*, 1963, **88**, 76.
8. *Idem, ibid.*, 1968, **93**, 461.
9. M. S. Frant and J. W. Ross, *Anal. Chem.*, 1968, **46**, 1169.
10. C. R. Edmond, *ibid.*, 1969, **41**, 1327.
11. E. J. Duff and J. L. Stuart, *Anal. Chim. Acta*, 1970, **52**, 155.
12. J. L. Stuart, *Analyst*, 1970, **95**, 1032.
13. K. Srinivasin and G. A. Rechnitz, *Anal. Chem.*, 1968, **40**, 509.
14. *Idem, ibid.*, 1968, **40**, 818.
15. F. M. Hall and S. J. Slater, *Aust. J. Chem.*, 1968, **21**, 2663.
16. A. M. Bond and T. A. O'Donnell, *J. Electroanal. Chem.*, 1970, **26**, 137.
17. M. N. Hughes and K. J. Rutt, *J. Chem. Soc. (A)*, 1968, 2788.
18. E. J. Duff, *J. Inorg. Nucl. Chem.*, submitted for publication.
19. *Idem, J. Chem. Soc. (A)*, 1971, 33.

Talanta, 1972, Vol. 19, pp. 80 to 82. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in coke by the oxygen-flask method

(*Received* 12 *January* 1971. *Accepted* 13 *July* 1971)

EARLIER[1] we described the determination of phosphorus in coke by oxygen-flask combustion followed by the method described in B.S. 1016 Part 9.[2] More recently a new reagent was proposed for the reduction of phosphomolybdate[3] and applied to the determination of phosphorus in coal,[4,5] the novel feature being reduction of phosphomolybdate by ascorbic acid, with potassium antimonyl tartrate as catalyst, the reagents being combined in a single solution. This paper shows how these developments were combined for determination of phosphorus in coke.

EXPERIMENTAL

Preliminary studies of the reducing agent suggested by Shafran *et al.*[3] led to minor modifications of the method, involving daily preparation of fresh batches of reagent solution, and an increase to 20 min in the time allowed for development of the colour.

A comparison was then made of the results obtained by the British Standard method[2] and the modified method using the catalysed ascorbic acid reagent. The mean results of duplicate tests are given in Table I for a series of commercially produced high-temperature metallurgical cokes. The phosphorus was extracted from the ash by the British Standard method.

TABLE I.—COMPARISON OF METHODS FOR THE DETERMINATION OF PHOSPHORUS IN COKE

Sample	Phosphorus content of coke, %		
	B.S. method[2] (*A*)	Proposed method (*B*)	Difference, $A - B$
1	0·0157	0·0155	+0·0002
2	0·0126	0·0120	+0·0006
3	0·0111	0·0106	+0·0005
4	0·0106	0·0109	−0·0003
5	0·0098	0·0100	−0·0002
6	0·0079	0·0080	−0·0001
7	0·0073	0·0071	+0·0002
8	0·0065	0·0067	−0·0002
9	0·0047	0·0045	+0·0002
10	0·0029	0·0031	−0·0002

REFERENCES

1. M. S. Frant and J. W. Ross, *Science*, 1966, **154**, 1553.
2. see *Ion Selective Electrodes*, ed. R. A. Durst, *Natl. Bur. Stds. Monograph* 314, 1969.
3. H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 784.
4. H. W. Wharton, *Anal. Chem.*, 1962, **34**, 296.
5. S. A. Leach and W. D. Armstrong, *Arch. Oral Biol.*, 1963, **8**, 81.
6. L. Singer and W. D. Armstrong, *Anal. Chem.*, 1959, **31**, 105.
7. R. J. Hall, *Analyst*, 1963, **88**, 76.
8. *Idem, ibid.*, 1968, **93**, 461.
9. M. S. Frant and J. W. Ross, *Anal. Chem.*, 1968, **46**, 1169.
10. C. R. Edmond, *ibid.*, 1969, **41**, 1327.
11. E. J. Duff and J. L. Stuart, *Anal. Chim. Acta*, 1970, **52**, 155.
12. J. L. Stuart, *Analyst*, 1970, **95**, 1032.
13. K. Srinivasin and G. A. Rechnitz, *Anal. Chem.*, 1968, **40**, 509.
14. *Idem, ibid.*, 1968, **40**, 818.
15. F. M. Hall and S. J. Slater, *Aust. J. Chem.*, 1968, **21**, 2663.
16. A. M. Bond and T. A. O'Donnell, *J. Electroanal. Chem.*, 1970, **26**, 137.
17. M. N. Hughes and K. J. Rutt, *J. Chem. Soc.* (*A*), 1968, 2788.
18. E. J. Duff, *J. Inorg. Nucl. Chem.*, submitted for publication.
19. *Idem, J. Chem. Soc.* (*A*), 1971, 33.

Talanta, 1972, Vol. 19, pp. 80 to 82. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in coke by the oxygen-flask method

(*Received* 12 *January* 1971. *Accepted* 13 *July* 1971)

EARLIER[1] we described the determination of phosphorus in coke by oxygen-flask combustion followed by the method described in B.S. 1016 Part 9.[2] More recently a new reagent was proposed for the reduction of phosphomolybdate[3] and applied to the determination of phosphorus in coal,[4,5] the novel feature being reduction of phosphomolybdate by ascorbic acid, with potassium antimonyl tartrate as catalyst, the reagents being combined in a single solution. This paper shows how these developments were combined for determination of phosphorus in coke.

EXPERIMENTAL

Preliminary studies of the reducing agent suggested by Shafran *et al.*[3] led to minor modifications of the method, involving daily preparation of fresh batches of reagent solution, and an increase to 20 min in the time allowed for development of the colour.

A comparison was then made of the results obtained by the British Standard method[2] and the modified method using the catalysed ascorbic acid reagent. The mean results of duplicate tests are given in Table I for a series of commercially produced high-temperature metallurgical cokes. The phosphorus was extracted from the ash by the British Standard method.

TABLE I.—COMPARISON OF METHODS FOR THE DETERMINATION OF PHOSPHORUS IN COKE

Sample	Phosphorus content of coke, %		
	B.S. method[2] (*A*)	Proposed method (*B*)	Difference, *A* − *B*
1	0·0157	0·0155	+0·0002
2	0·0126	0·0120	+0·0006
3	0·0111	0·0106	+0·0005
4	0·0106	0·0109	−0·0003
5	0·0098	0·0100	−0·0002
6	0·0079	0·0080	−0·0001
7	0·0073	0·0071	+0·0002
8	0·0065	0·0067	−0·0002
9	0·0047	0·0045	+0·0002
10	0·0029	0·0031	−0·0002

It was concluded that the proposed reducing agent functioned successfully. Because of the volume of the $1N$ sulphuric acid used as absorbent in the flask-combustion method it was necessary to reduce the concentration of the acid used in the preparation of the reagent solution.

Reagents

Sulphuric acid, $5N$.

Ammonium molybdate solution, 6% w/v.

Ascorbic acid solution, 5% w/v.

Potassium antimonyl tartrate solution. Dissolve 0·34 g of reagent in 250 ml of water.

Reagent solution. Mix 125 ml of the sulphuric acid, 50 ml of the ammonium molybdate solution, 50 ml of the ascorbic acid solution and 25 ml of the antimony potassium tartrate solution. Prepare freshly each day before use.

Standard phosphorus solution. Dissolve 0·4392 g of potassium dihydrogen phosphate (dried at 110° for 1 hr) in water and dilute to 1 litre. Dilute 20 ml of this standard solution to 1 litre with water to obtain the working solution, which contains 2 μg of phosphorus/ml.

Eschka mixture. Analytical reagent quality.

Apparatus

A 250-ml combustion flask, fitted with a B24 stopper carrying a platinum wire 60 mm long and 1 mm in diameter. The sample carrier attached to the platinum wire is 20 mm long and 7·5 mm in diameter, fabricated from 36-mesh (422-μm) platinum gauze.

Procedure

Mix intimately 30 mg of coke, ground to pass a 240-mesh (63-μm) test-sieve with approximately 30 mg of Eschka mixture, wrap the mixture in filter paper and burn it in the oxygen flask, which contains 10 ml of $1N$ sulphuric acid as absorbent. Shake to absorb combustion products, wash the platinum basket with distilled water, boil the solution for a few min, cool and filter into a 50-ml standard flask. Dilute to 35 ml with distilled water, add 5 ml of fresh reagent solution by pipette, swirling the flask during the addition, dilute to the mark with distilled water, shake and stand for 20 min. Measure the absorbance at 680–710 nm in 40-mm cells against distilled water.

Run a blank determination and apply an appropriate correction.

RESULTS

Table II compares the mean values of duplicate determinations by the present standard method and the new method. The same operator carried out all the determinations.

The within-laboratory tolerance of the determination (95% limits) is 0·0013% phosphorus. The corresponding value for the tests carried out by the B.S. method was 0·0010%. These limits are

TABLE II.—COMPARISON OF THE PHOSPHORUS CONTENT OF COKE DETERMINED BY THE STANDARD METHOD AND BY OXYGEN-FLASK COMBUSTION USING P.A.T. REAGENT

Sample	Phosphorus content of coke, %		
	B.S. method[2] (A)	Flask combustion and new reagent (B)	Difference, $A - B$
11	0·0657	0·0663	−0·0006
12	0·0476	0·0476	nil
13	0·0322	0·0319	+0·0003
14	0·0261	0·0258	+0·0003
15	0·0245	0·0246	−0·0001
16	0·0211	0·0224	−0·0013
17	0·0162	0·0168	−0·0006
1	0·0157	0·0162	−0·0005
18	0·0144	0·0135	+0·0009
2	0·0126	0·0123	+0·0003
19	0·0070	0·0079	−0·0009
8	0·0067	0·0069	−0·0002

within those adopted in the current British Standard (0·002% for cokes with a phosphorus content of $\leqslant 0{\cdot}02\%$, or 10% of phosphorus content $>0{\cdot}02\%$.)

The method is shorter, simpler and cheaper than that described in the present standard and is thus suitable for use in control or plant laboratories. The technique of reducing phosphomolybdate by ascorbic acid, with potassium antimonyl tartrate as catalyst in a single solution has been adopted in the revised version of the B.S. method for the determination of phosphorus in coal and coke.[6]

Acknowledgement—This work formed part of the programme of research of the British Coke Research Association. We are indebted to the Director for permission to publish this paper.

B. P. Kirk
H. C. Wilkinson

British Coke Research Association
Coke Research Centre
Chesterfield, Derbyshire

Summary—Recent developments in the oxygen-flask technique for determination of phosphorus in coke are described. The existing method was modified by use of the recently proposed potassium antimonyl tartrate catalyst for the ascorbic acid reduction of phosphomolybdate.

Zusammenfassung—Neue Entwicklungen beim Sauerstoffkolben-Verfahren zur Bestimmung von Phosphor in Koks werden mitgeteilt. Das bestehende Verfahren wurde durch Verwendung des jüngst vorgeschlagenen Kaliumantimonyltartrat-Katalysators bei der Reduktion von Phosphomolybdat mit Ascorbinsäure modifiziert.

Résumé—On décrit les développements récents de la technique de la fiole d'oxygéne pour le dosage du phosphore dans le coke. On a modifié la méthode existante par l'emploi du catalyseur tartrate d'antimonyle et de potassium récemment proposé pour la réduction du phosphomolybdate par l'acide ascorbique.

REFERENCES

1. B. P. Kirk and H. C. Wilkinson, *Fuel, London*, 1964, 43, 105.
2. British Standards Institution. *Methods for the analysis and testing of coal and coke. Phosphorus in coal and coke.* B.S. 1016: Part 9: 1960.
3. I. G. Shafran, M. V. Pavlova, S. A. Titova, L. D. Yakushava. *Tr. Vses. Nauch-Issled. Inst. Khim. Reakt.* 1966, 66. *Anal. Abstr.*, 1967, **14**, 6767.
4. Private communication, The British Coal Utilisation Research Association.
5. Private communication, National Coal Board, Scientific Control.
6. See Ref. 2. Revised edition (Metric Units) B.S. 1016: Part 9: 1971.

Talanta, 1972, Vol. 19, pp. 82 to 87. Pergamon Press. Printed in Northern Ireland

Spectrophotometric study of the determination of copper with ammonium 1-pyrrolidinecarbodithioate

(*Received* 3 *December* 1970. *Accepted* 3 *August* 1971)

A NUMBER of chromogenic agents have been proposed for the determination of micro amounts of copper. Dithizone gives a sensitive colour reaction but is not very specific.[1,2] Cuproine, 2,2′-biquinoline, is a more specific reagent for copper but is less sensitive.[3,4] Neocuproine, 2,9-dimethyl-1,10-phenanthroline, reacts with copper(I) to form an extractable metal chelate with a molar within those adopted in the current British Standard (0·002% for cokes with a phosphorus content of $\leqslant$0·02%, or 10% of phosphorus content >0·02%.)

The method is shorter, simpler and cheaper than that described in the present standard and is thus suitable for use in control or plant laboratories. The technique of reducing phosphomolybdate by ascorbic acid, with potassium antimonyl tartrate as catalyst in a single solution has been adopted in the revised version of the B.S. method for the determination of phosphorus in coal and coke.[6]

Acknowledgement—This work formed part of the programme of research of the British Coke Research Association. We are indebted to the Director for permission to publish this paper.

B. P. Kirk
H. C. Wilkinson

British Coke Research Association
Coke Research Centre
Chesterfield, Derbyshire

Summary—Recent developments in the oxygen-flask technique for determination of phosphorus in coke are described. The existing method was modified by use of the recently proposed potassium antimonyl tartrate catalyst for the ascorbic acid reduction of phosphomolybdate.

Zusammenfassung—Neue Entwicklungen beim Sauerstoffkolben-Verfahren zur Bestimmung von Phosphor in Koks werden mitgeteilt. Das bestehende Verfahren wurde durch Verwendung des jüngst vorgeschlagenen Kaliumantimonyltartrat-Katalysators bei der Reduktion von Phosphomolybdat mit Ascorbinsäure modifiziert.

Résumé—On décrit les développements récents de la technique de la fiole d'oxygéne pour le dosage du phosphore dans le coke. On a modifié la méthode existante par l'emploi du catalyseur tartrate d'antimonyle et de potassium récemment proposé pour la réduction du phosphomolybdate par l'acide ascorbique.

REFERENCES

1. B. P. Kirk and H. C. Wilkinson, *Fuel, London*, 1964, 43, 105.
2. British Standards Institution. *Methods for the analysis and testing of coal and coke. Phosphorus in coal and coke.* B.S. 1016: Part 9: 1960.
3. I. G. Shafran, M. V. Pavlova, S. A. Titova, L. D. Yakushava. *Tr. Vses. Nauch-Issled. Inst. Khim. Reakt.* 1966, 66. *Anal. Abstr.*, 1967, **14**, 6767.
4. Private communication, The British Coal Utilisation Research Association.
5. Private communication, National Coal Board, Scientific Control.
6. See Ref. 2. Revised edition (Metric Units) B.S. 1016: Part 9: 1971.

Talanta, 1972, Vol. 19, pp. 82 to 87. Pergamon Press. Printed in Northern Ireland

Spectrophotometric study of the determination of copper with ammonium 1-pyrrolidinecarbodithioate

(*Received* 3 *December* 1970. *Accepted* 3 *August* 1971)

A NUMBER of chromogenic agents have been proposed for the determination of micro amounts of copper. Dithizone gives a sensitive colour reaction but is not very specific.[1,2] Cuproine, 2,2′-biquinoline, is a more specific reagent for copper but is less sensitive.[3,4] Neocuproine, 2,9-dimethyl-1,10-phenanthroline, reacts with copper(I) to form an extractable metal chelate with a molar absorptivity of 7·95 × 10^2 l.mole^{-1}.mm^{-1}.[5] The copper(I) chelates of several bipyridyl derivatives have been studied: 6,6'-dimethyl-2,2'-bipyridine;[6] 2,6-bis(6-phenyl-2-pyridyl)-4-phenylpyridine;[7] and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, bathocuproine.[8]

One of the most widely used spectrophotometric reagents for copper is sodium diethyldithiocarbamate which forms an extractable complex exhibiting a molar absorptivity of 1·3 × 10^3 l.mole^{-1}.mm^{-1}.[9,10]

The main disadvantages of this reagent are its instability in acidic media and lack of specificity. However, the deleterious effect of many metals can be circumvented by masking the interfering cations with EDTA.[11] Zinc dibenzyldithiocarbamate has been used as an alternative reagent because it is more stable in acidic solutions and shows less interference by iron(III) and several other ions.[12,13] The extensive use of ammonium 1-pyrrolidinecarbodithioate, often designated ammonium pyrrolidinedithiocarbamate, as an extractant for copper before the determination of copper by atomic-absorption spectrometry,[14–16] and the superiority of this reagent in the ultraviolet spectrophotometric determination of cadmium, cobalt and bismuth,[17] resulted in the spectrophotometric study of the copper(II)–1-pyrrolidinecarbodithioate system. The proposed method is selective and more sensitive when ultraviolet absorbance measurements are made. The reagent is more stable, especially in acidic solutions, than its diethyl analogue.

EXPERIMENTAL

Reagents

Standard copper(II) *solution.* Transfer 0·1000 g of reagent grade copper metal to a small conical flask and add 3–5 ml of concentrated nitric acid to effect dissolution. Add 10–15 ml of water and heat to boiling. Rinse the inside of the flask with 10–15 ml of water and heat again to boiling to expel oxides of nitrogen. Transfer this solution and several rinsings of the flask to a 1-litre volumetric flask and dilute to volume with water. A tenfold dilution of this stock solution gives a standard solution containing 10·0 μg of copper per ml.

Ammonium 1-pyrrolidinecarbodithioate (APCDT) regent solution. Dissolve 0·150 g of pure ammonium 1-pyrrolidinecarbodithioate in 100 ml of water containing 0·1–0·3 ml of ammonia solution (1 + 1). Filter and store in an amber glass bottle. The reagent is stable for at least two weeks.

Acetate buffer solution. Dissolve 12·3 g of sodium acetate trihydrate in distilled water. Add 5·0 ml of glacial acetic acid and dilute to 1 litre with distilled water. The pH of this buffer solution is 4·7.

Phosphate buffer solution. Dissolve 0·40 g of potassium dihydrogen phosphate in approximately 900 ml of distilled water. Add sufficient potassium monohydrogen phosphate to adjust the pH to 8·0 and dilute to 1 litre.

Procedure

Transfer 10 ml of buffer solution to a 60-ml separatory funnel. (Use phosphate buffer if absorbance measurements are to be made at 269 nm; use the acetate buffer if absorbance measurements are to be made at 435 nm.) Add the sample solution containing about 1–80 μg of copper(II). Add 5 ml of the 0·15% APCDT solution, mix and allow to stand for 5 min. Add 10 ml of chloroform and shake vigorously for 1 min in a mechanical shaker. Prepare a reference blank solution by the same procedure but using distilled water instead of the sample solution (use the same total volume). Measure the absorbance at 269 nm (phosphate buffer) or 435 nm (acetate buffer) in 10-mm silica cells.

RESULTS AND DISCUSSION

Absorption spectra

Aqueous solutions of ammonium 1-pyrrolidinecarbodithioate exhibit ultraviolet absorbance maxima at 254,277 and 336 mn, whereas the chloroform extract of the reagent exhibits absorbance maxima at 280 nm and 336 nm. Absorbance maxima for the copper(II)–1-pyrrolidinecarbodithioate complex were found at 269 nm and 435 nm. Figure 1 shows the characteristic absorption spectrum of the copper–PCDT–chloroform system as measured against a chloroform extract of a reagent blank solution.

Effect of solution variables

Concentration of copper. Conformity to Beer's law was observed over a concentration range of 0·1–8 ppm of copper. The optimum concentration range is 0·2–4·0 μg of copper per ml when the phosphate buffer is used and the absorbance is measured at 269 nm and 0·4–4·0 μg of copper per ml when the acetate buffer is used and the absorbance is measured at 435 nm.

Concentration of reagent. The effect of adding varying amounts of the 0·15% APCDT solution to a solution containing 2 μg of copper per ml showed that when absorbance measurements were made at 435 nm the absorbance did not change when the mole ratio of reagent to copper varied from 6 : 1 to 240 : 1. The fact that the reagent does not absorb at 435 nm means that the exact amount of reagent used is not critical. Therefore, the 5 ml of 0·15% reagent used in the procedure provides for about a 20–30-fold excess of reagent for the highest concentration of copper which can be determined by this method. Because the reagent does absorb at 269 nm careful control of the concentration of the reagent is essential when this wavelength is used and necessitates the use of a reagent blank solution in the reference cell. Thus, the higher sensitivity achieved by making absorbance measurements at 269 nm is accompanied by some loss in precision because of slight variations in reagent concentration.

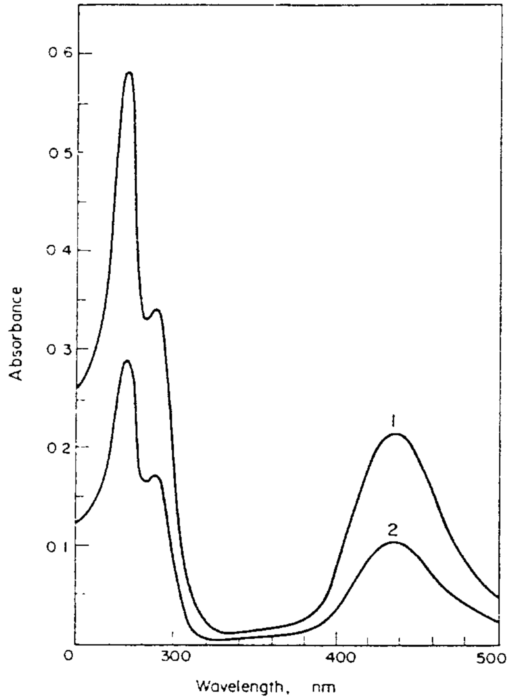


Fig. 1.–Characteristic absorption spectra for the Cu-PCDT complex in chloroform.
1. Copper 1 μg/ml
2. Copper 0·5 μg/ml

pH. The results of a study of the effect of pH on the determination of 2 μg of copper per ml showed that at pH of 4, 5, 6, 7, 8 and 9·5 the corresponding absorbance values at 435 nm were 0·429, 0·422, 0·422, 0·422, 0·420 and 0·418. Hence control of pH is not critical in the range 4–9·5, which is useful for trying to mask certain interfering ions. However, if the absorbance measurements are to be made at 269 nm, it is necessary to use the basic phosphate buffer solution because in acidic media the extraction of reagent is excessive and causes difficulty in using the external compensation technique of spectrophotometric measurement.

Extraction time. The effect of shaking time on the efficiency of the extraction was studied. When shaking times of 30, 45, 60, 90 and 120 sec were used the corresponding absorbances obtained were 0·419, 0·423, 0·423, 0·422 and 0·420. An extraction time of one minute was selected as being optimum. The volume of chloroform used is not critical, because of the very favourable distribution ratio for the copper(II)-PCDT system. Although the use of 10 ml of chloroform is designated in the recommended general procedure, the use of 5 ml of chloroform was found to be equally efficient and is recommended if less than 0·5 μg of copper is to be determined.

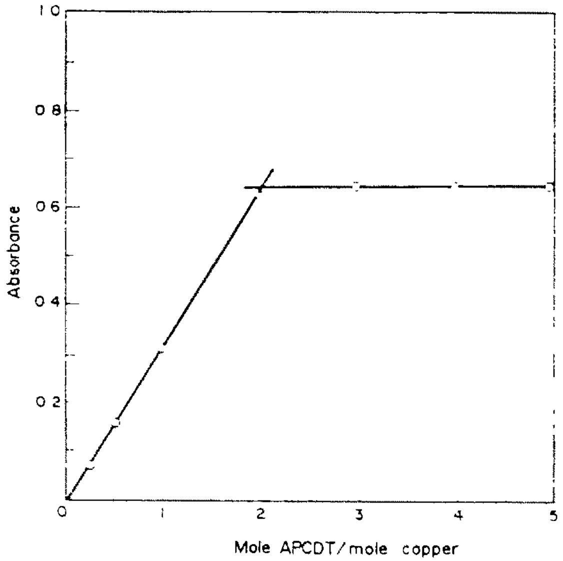


FIG. 2—Mole-ratio plot for the Cu-PCDT complex.

TABLE I.—INTERFERING IONS

Ion	Conc., *ppm*	Relative error, %	Permissible amount*, *ppm*
Bi^{3+}	10	30	6
Cd^{2+}	50	52	10
Co^{2+}	5	>100	0
Fe^{2+}	5	>100	0
Fe^{3+}	5	>100	0
Mn^{2+}	60	30	10
Hg^{2+}	500	>100	80
MoO_4^{2-}	5	9	2
Ni^{2+}	5	19	0
Sn^{2+}	50	13	10
SeO_3^{2-}	50	14	15
VO_3^-	5	5	2
Zn^{2+}	500	>100	80
In the presence of 1000 ppm EDTA + 500 ppm tartrate			
Bi^{3+}	50	>100	—
Co^{2+}	50	28	—
Cd^{2+}	50	−5	40
Sn^{2+}	50	38	—
Mn^{2+}	50	0	100
Ni^{2+}	100	0	100
Using 5 ml 0·015% APCDT			
Bi^{3+}	50	45	
Co^{2+}	50	0	50
Fe^{3+}	50	0	50

* Causes an error of less than three times the standard deviation with 2·0 ppm of copper.

Composition of the complex

A study of the composition of the copper (II)–PCDT system was made by the mole-ratio method. A $4{\cdot}7 \times 10^{-7}M$ copper (II) solution and a $4{\cdot}7 \times 10^{-4}M$ reagent solution were used with absorbance being measured at 435 nm. As shown in Fig. 2 a 1 : 2 ratio was obtained for the Cu–PCDT complex.

Effect of diverse ions

A concentration of 500 ppm of the following anions caused no interference in the determination of 2 ppm of copper when absorbance measurements were made at 435 nm: acetate, bromide, carbonate, chloride, iodide, fluoride, molybdate, nitrate, perchlorate, phosphate, thiocyanate, silicate, sulphate, sulphite, selenite, vanadate, tungstate, tartrate and EDTA. Of the cations tested, the following can be tolerated at 500-ppm level: ammonium, aluminium, barium, calcium, magnesium, potassium and sodium.

Table I shows those ions which caused an error larger than 3 times the relative standard deviation when present at 500-ppm concentration. Most of the interfering ions form chelates with the excess of reagent. Although these other metal–PCDT complexes may have absorbance maxima considerably removed from that of the copper-PCDT system, interference results at relatively high concentrations of the diverse ion. Interference may be circumvented by the control of pH, the use of masking agents and by using a lower concentration of the reagent so that less of the interfering metal chelate is formed.

Precision

A statistical study of the 435-nm method was made to estimate the precision. Ten independent determinations on solutions containing 2·5 μg of copper per ml gave a mean absorbance value of 0·520, and a standard deviation of $3{\cdot}8 \times 10^{-3}$ absorbance unit or relative standard deviation of 0·7%. A similar statistical study of 6 independent determinations of the reagent blank solution gave a mean absorbance of 0·044, and a standard deviation of $2{\cdot}0 \times 10^{-3}$ absorbance unit or relative standard deviation of 4·7%

Sensitivity and detection limit

The molar absorptivities for the copper(II)–PCDT–chloroform system is $1{\cdot}35 \times 10^{3}$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 435 nm and $3{\cdot}4 \times 10^{3}$ $\text{l.mole}^{-1}\text{mm}^{-1}$ at 269 nm. The detection limit based on Kaiser's[18] recommended criteria is 0·03 μg of copper when absorbance is measured at 435 nm.

Department of Chemistry
Wayne State University
Detroit
Michigan 48202, *U.S.A.*

R. W. Looyenga*
D. F. Boltz

Summary—A new spectrophotometric method for the determination of traces of copper has been developed. The method is based on the formation of a stable 1:2 complex of copper(II) and 1-pyrrolidinecarbodithioate and the isolation of this complex by extraction into chloroform. The absorbance is measured at either 269 nm or 435 nm. The detection limit is 0·03 μg of copper per ml for absorbance measurements at 435 nm.

Zusammenfassung—Ein neues spectrophotometrisches Verfahren zur Bestimmung von Kupferspuren wurde entwickelt. Es beruht auf der Bildung eines stabilen 1:2-Komplexes aus Kupfer(II) und 1-Pyrrolidincarbodithioat und der Isolierung dieses Komplexes durch Extraktion in Chloroform. Die Extinktion wird entweder bei 269 nm oder bei 435 nm gemessen. Die Nachweisgrenze beträgt 0,03 μg Kupfer pro ml, wenn die Extinktion bei 435 nm gemessen wird.

Résumé—On a élaboré une nouvelle méthode spectrophotometrique pour le dosage de traces de cuivre. La methode est basée sur la formation d'un complexe stable 1:2 entre le cuivre et le 1-pyrrolidine carbodithioate, et l'isolement de ce complexe par extraction en chloroforme. On mesure l'absorption à 269 ou à 435 nm. La limite de détection est de 0,03 μg de cuivre par ml pour les mesures d'absorption à 435 nm.

---

* Present Address: Printing Developments Inc., Racine, Wisconsin.

REFERENCES

1. E. A. Brown, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 493.
2. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, *3rd Ed.*, p. 453. Interscience, New York, 1959.
3. J. Hoste, J. Eeckhout and J. Gillis, *Anal. Chim. Acta*, 1953, **9**, 263.
4. R J. Guest, *Anal. Chem.*, 1953, **25**, 1484.
5. G. F. Smith and W. H. McCurdy, *ibid*, 1952, **24**, 371.
6. J. Hoste, *Anal. Chim. Acta*, 1955, **4**, 23.
7. A. A. Schilt and G. F. Smith, *ibid*, 1956, **15**, 561.
8. G. F. Smith and D. H. Wilkins, *Anal. Chem.*, 1953, **25**, 510.
9. H. Bode. *Z. Anal. Chem.*, 1955, **144**, 165.
10. H. Malissa, *Anal. Chim. Acta*, 1962, **27**, 402.
11. A. Claassen and L. Bastings, *Z. Anal. Chem.*, 1956, **153**, 30.
12. R. I. Martens and R. E. Githens, *Anal. Chem.*, 1952, **24**, 991.
13. O. P. Bhargava, *Talanta*, 1969, **16**, 743.
14. J. E. Allan, *Spectrochim. Acta*, 1961, **17**, 459.
15. M. E. Morgan, Atomic *Absorption Newsletter*, 1964, **3**, 21.
16. D. J. Trent and W. Slavin, *ibid*, 1964, **3**, 118.
17. M. B. Kalt and D. F. Boltz, *Anal. Chem.*, 1968, **40**, 1086.
18. H. Kaiser, *ibid*, 1970, **42**, No. 4, 26A.

Talanta, 1972, Vol. 19, pp. 87 to 92. Pergamon Press. Printed in Northern Ireland

Stabilities of some cyclopentadienide metal complexes

(*Received* 11 *June* 1971. *Accepted* 21 *August* 1971)

During the last two decades the metal complexes of cyclopentadienide have been intensively studied in connection with the problems of organometallic chemistry.[1] For that reason, it may be of some interest to determine the stability of those complexes in solution.

EXPERIMENTAL

Reagents

Preparation of cyclopentadiene. Add dropwise sodium cyclopentadienide to a cooled (−5° to 0°) well stirred solution of 3*M* sulphuric acid. Separate the organic layer, dry it with anhydrous sodium sulphate and distil under normal pressure in an atmosphere of nitrogen. Collect the 39–41° fraction. Store the product in the dark in a solid carbon dioxide bath.

When stored under the given conditions, the product is stable for 2–3 weeks. The quality of the product was checked by measurement of the refractive index $n_D^{25°} = 1{\cdot}4471$ (1·4404) and density $d_D^{25°} = 0{\cdot}7969$ (0·7966). The values in brackets are due to Raistrik *et al.*[2]

To avoid the oxidation of cyclopentadiene and ions of iron(II), manganese(II) and cobalt(II), all solutions (including the buffer solutions) were prepared in a nitrogen atmosphere from solvents from which oxygen had been removed by distillation in nitrogen. Ethanolic and dimethylformamide solutions of cyclopentadiene ($1{\cdot}00 \times 10^{-2}M$) were prepared daily.

Metal ion solutions. The aqueous and dimethylformamide solutions of metal chlorides were $1{\cdot}00 \times 10^{-2}M$.

Buffers solutions. The pH was adjusted by means of borax and perchloric acid (pH 7·20–9·01), borax and sodium hydroxide (pH 9·26–10·82), and sodium hydroxide (pH 10·93–15·80). The ionic strength between pH 7·20 and 12·95 was kept constant (0·10*M*) by means of sodium perchlorate.[3] The data of Schwarzenbach and Sulzberger[4] were used to establish pH 13·00–15·80. The nitrogen used was washed with 10% chromium(II) chloride solution.

Measurement

A nitrogen atmosphere was used for the preparation of solutions to be measured and for the absorbance measurements. The sequence reagent, metal ion and buffer was adhered to during the preparation of all measured solutions; the temperature was kept at 25±1°. The absorbance of solutions was measured against a solvent–buffer blank.

REFERENCES

1. E. A. Brown, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 493.
2. E. B. Sandell, *Colorimetric Determination of Traces of Metals, 3rd Ed.*, p. 453. Interscience, New York, 1959.
3. J. Hoste, J. Eeckhout and J. Gillis, *Anal. Chim. Acta*, 1953, **9**, 263.
4. R. J. Guest, *Anal. Chem.*, 1953, **25**, 1484.
5. G. F. Smith and W. H. McCurdy, *ibid*, 1952, **24**, 371.
6. J. Hoste, *Anal. Chim. Acta*, 1955, **4**, 23.
7. A. A. Schilt and G. F. Smith, *ibid*, 1956, **15**, 561.
8. G. F. Smith and D. H. Wilkins, *Anal. Chem.*, 1953, **25**, 510.
9. H. Bode. *Z. Anal. Chem.*, 1955, **144**, 165.
10. H. Malissa, *Anal. Chim. Acta*, 1962, **27**, 402.
11. A. Claassen and L. Bastings, *Z. Anal. Chem.*, 1956, **153**, 30.
12. R. I. Martens and R. E. Githens, *Anal. Chem.*, 1952, **24**, 991.
13. O. P. Bhargava, *Talanta*, 1969, **16**, 743.
14. J. E. Allan, *Spectrochim. Acta*, 1961, **17**, 459.
15. M. E. Morgan, Atomic *Absorption Newsletter*, 1964, **3**, 21.
16. D. J. Trent and W. Slavin, *ibid*, 1964, **3**, 118.
17. M. B. Kalt and D. F. Boltz, *Anal. Chem.*, 1968, **40**, 1086.
18. H. Kaiser, *ibid*, 1970, **42**, No. 4, 26A.

Talanta, 1972, Vol. 19, pp. 87 to 92. Pergamon Press. Printed in Northern Ireland

Stabilities of some cyclopentadienide metal complexes

(*Received* 11 *June* 1971. *Accepted* 21 *August* 1971)

DURING the last two decades the metal complexes of cyclopentadienide have been intensively studied in connection with the problems of organometallic chemistry.[1] For that reason, it may be of some interest to determine the stability of those complexes in solution.

EXPERIMENTAL

Reagents

Preparation of cyclopentadiene. Add dropwise sodium cyclopentadienide to a cooled (−5° to 0°) well stirred solution of $3M$ sulphuric acid. Separate the organic layer, dry it with anhydrous sodium sulphate and distil under normal pressure in an atmosphere of nitrogen. Collect the 39–41° fraction. Store the product in the dark in a solid carbon dioxide bath.

When stored under the given conditions, the product is stable for 2–3 weeks. The quality of the product was checked by measurement of the refractive index $n_D^{25°} = 1{\cdot}4471$ (1·4404) and density $d_D^{25°} = 0{\cdot}7969$ (0·7966). The values in brackets are due to Raistrik *et al.*[2]

To avoid the oxidation of cyclopentadiene and ions of iron(II), manganese(II) and cobalt(II), all solutions (including the buffer solutions) were prepared in a nitrogen atmosphere from solvents from which oxygen had been removed by distillation in nitrogen. Ethanolic and dimethylformamide solutions of cyclopentadiene ($1{\cdot}00 \times 10^{-2}M$) were prepared daily.

Metal ion solutions. The aqueous and dimethylformamide solutions of metal chlorides were $1{\cdot}00 \times 10^{-2}M$.

Buffers solutions. The pH was adjusted by means of borax and perchloric acid (pH 7·20–9·01), borax and sodium hydroxide (pH 9·26–10·82), and sodium hydroxide (pH 10·93–15·80). The ionic strength between pH 7·20 and 12·95 was kept constant (0·10M) by means of sodium perchlorate.[3] The data of Schwarzenbach and Sulzberger[4] were used to establish pH 13·00–15·80. The nitrogen used was washed with 10% chromium(II) chloride solution.

Measurement

A nitrogen atmosphere was used for the preparation of solutions to be measured and for the absorbance measurements. The sequence reagent, metal ion and buffer was adhered to during the preparation of all measured solutions; the temperature was kept at 25 ± 1°. The absorbance of solutions was measured against a solvent–buffer blank.

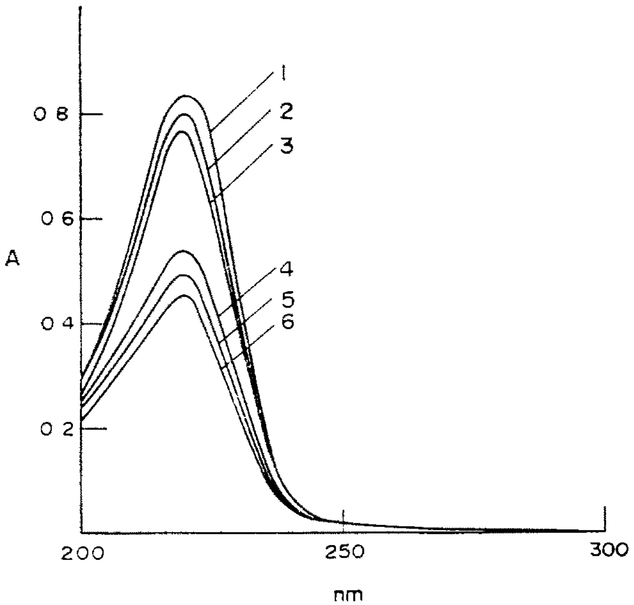


FIG. 1.—Absorption spectra of iron(II) (1), manganese(II) (2), cobalt(II) (3), palladium(II) (4) and nickel(II) (5) complexes of cyclopentadienide in aqueous solution. $2c_M = c_L = 4{\cdot}00 \times 10^{-5}M$ and pH 12·70 where c_M and c_L are the total concentrations of metal and cyclopentadiene respectively. Curve 6 is the reagent alone at pH 14·80.

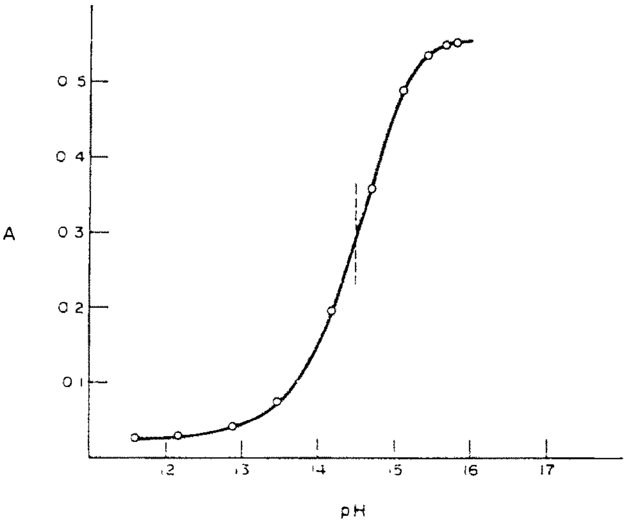


FIG. 2.—Dependence of cyclopentadiene absorbance at 220 nm on pH $c_L = 4{\cdot}00 \times 10^{-5}M$.

TABLE I.—STABILITIES OF SOME COMPLEXES OF CYCLOPENTADIENIDE IN WATER AND DIMETHYLFORMAMIDE (DMF)†

Complex	Solvent (pH)	$\Delta A_1/\Delta A_2$‡	$\log K_n$	$\log \alpha_{M(OH)}$	$\log \alpha_{L(H)}$	$\log \beta_n$
HL	Water	—	—	—	—	14·5
MnL_2	12·70	2·840	8·5	2·1	1·9	14·4
	12·95	2·571	8·9	2·4	1·5	14·3
	13·50	2·386	9·3	2·9	1·0	14·2
FeL_2	7·89	7·802	5·7	0·0	6·6	18·9
	8·09	7·651	5·9	0·0	6·4	18·7
	8·23	7·106	6·4	0·0	6·3	19·0
CoL_2	11·79	7·996	4·6	2·5	2·7	12·5
	12·07	7·974	4·8	2·8	2·4	12·4
	12·39	7·914	5·3	3·1	2·1	12·6
NiL_2	12·70	7·998	3·3	3·3	1·9	10·4
	12·95	7·994	3·7	3·6	1·5	10·3
	13·50	7·992	4·3	4·2	1·0	10·5
PdL_2	12·70	4·910	7·3	—	—	—
	12·95	2·511	9·0	—	—	—
	13·50	2·094	10·9	—	—	—
$MnL(DMF)_x$	DMF	2·271	5·1	—	—	—
$FeL(DMF)_x$	DMF	2·244	5·2	—	—	—
$CoL(DMF)_x$	DMF	2·308	5·0	—	—	—
$NiL(DMF)_x$	DMF	2·552	4·5	—	—	—
$PdL(DMF_x$	DMF	2·692	4·3	—	—	—

† $c_M = 8{\cdot}00 \times 10^{-5} M$ throughout.

‡ $\Delta A = A - A_M - A_L$ where A is the absorbance of the solution with the complex, A_M and A_L are the absorbances of the metal ion and cyclopentadiene solution respectively. Subscript 1 refers to the basic total concentrations c_M, and c_L, subscript 2 to $c_M/2$ and $c_L/2$.

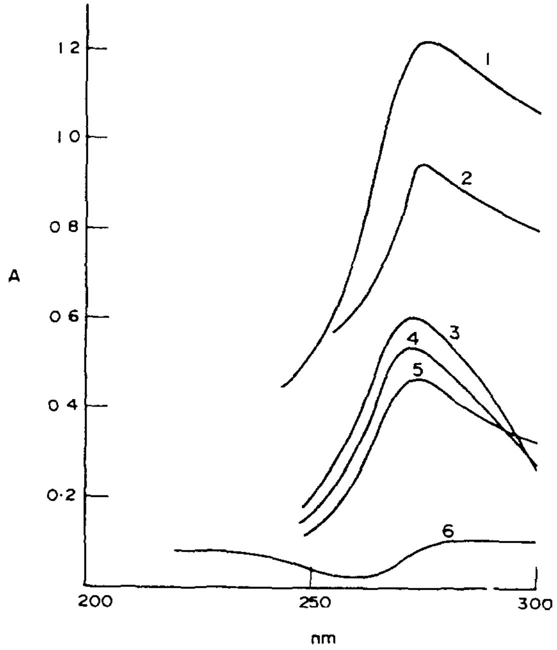


FIG. 3.—Absorption spectra of iron(II) (1), manganese(II) (2), cobalt(II) (3), palladium(II) (4) and nickel(II) (5) complexes of cyclopentadienide in dimethylformamide solution. Curve 6 is reagent alone.

$2c_M = c_L = 4{\cdot}00 \times 10^{-5} M$ was used throughout.

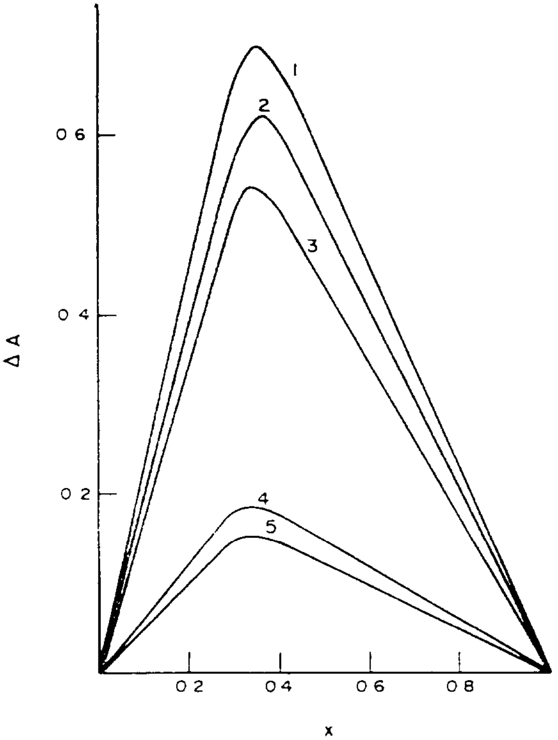


FIG. 4.—Continuous variation for iron(II) (1), manganese(II) (2), cobalt(II) (3), palladium(II) (4) and nickel(II) (5) with cyclopentadiene in aqueous solution. $c_M + c_L = 8{\cdot}00 \times 10^{-5}M$, $\lambda = 220$ nm, pH 12·07. The designation ΔA indicates that the absorbance was corrected for the absorption by cyclopentadiene and metal $x = c_M/(c_M + c_L)$.

RESULTS

Hydrogen complex

The stability of the hydrogen complex of cyclopentadienide was determined by the usual spectrophotometric method.[3] A typical absorption spectrum is shown in Fig. 1. The dependence of absorbance on pH is presented in Fig. 2. The value of the constant found is given in Table I.

Metal complexes

The dependence of complex formation on pH was investigated spectrophotometrically. Some representative absorption spectra in aqueous solution are given in Fig. 1. Spectra in dimethylformamide are shown in Fig. 3. The metal : ligand molar ratio of the complex was determined by the method of continous variation in equimolar solutions. Curves obtained are presented in Figs. 4 and 5. The effective stability constants K_n of the complexes were determined by the method of stoichiometric dilution.[5] From a set of effective stability constant values, the overall stability constant β_n was determined by means of the equation

$$\log \beta_n = \log K_n + \log \alpha_{M(OH)} + n \log \alpha_{L(H)} + j\,\text{pH} \qquad (1)$$

where $\alpha_{M(OH)}$ and $\alpha_{L(H)}$ designate the side-reaction coefficients of the metal with hydroxyl ions and of the ligand with hydrogen ions respectively. They are given by the equations

$$\alpha_{M(OH)} = 1 + \beta^*/[H] \qquad (2)$$

$$\alpha_{L(H)} = 1 + \beta_H[H] \qquad (3)$$

where

$$\beta^* = [M(OH)][H]/[M] \qquad (4)$$

$$\beta_H = [HL]/[H][L] \qquad (5)$$

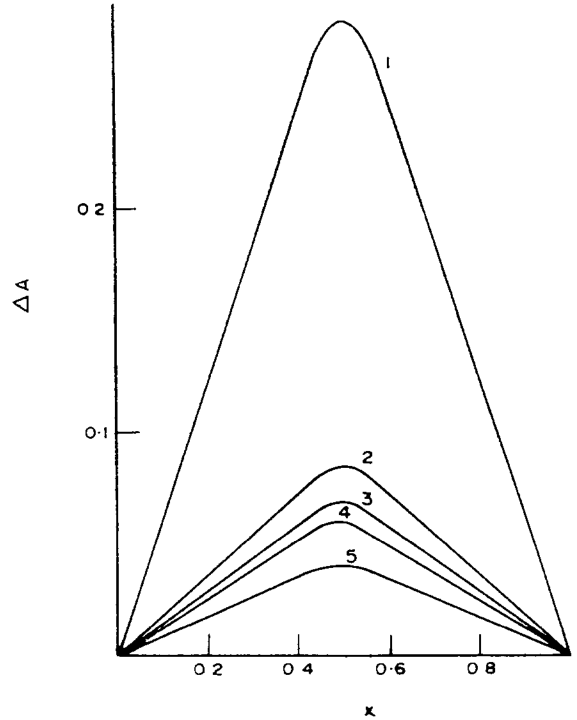


FIG. 5.—Continuous variation of iron(II) (1), manganese(II) (2), cobalt(II) (3), palladium(II) (4) and nickel(II) (5) with cyclopentadiene in dimethylformamide solution.

$c_M + c_L = 8{\cdot}00 \times 10^{-5}M$, $\lambda = 275$ nm. For ΔA and x see caption to Fig. 4.

The square brackets express the actual concentrations of the species. From possible complexes $M_i(OH)_i$ only the complex M(OH) was taken into account, owing to the low concentrations used. The values of β^* were taken from the monograph of Sillén and Martell.[7] The values of j designate the number of hydrogen ions in the complex MH_jL_n; L is the cyclopentadienide anion.

Results obtained are collected in Table I. They indicate that for metal complexes in aqueous solution j was always zero.

DISCUSSION

The value of the stability constant of the hydrogen complex of cyclopentadienide is in good agreement with previously estimated values.[8] Also the composition of cyclopentadienide metal complexes in aqueous solution is in agreement with the known data obtained by analysis of solid samples. However, the values of the effective stability constants show the relatively poor stability of the complexes in aqueous solution. The sequence of the values of overall stability constants indicates the adherence to the 18-electron rule, so an 18-electron complex has the maximum stability [complex of iron(II)] and with increasing deviation from that number there is a proportional decrease of stability of complexes.

It was impossible to determine the value of the overall stability constant of the palladium complex because of lack of data on palladium(II) hydrolysis.

The absorbance maximum of the iron(II) complex is in agreement with that measured for commercially available ferrocene. To prevent the hydrolysis of metal ions, the concentrations were kept as low as possible, therefore the far ultraviolet maxima were used, which occur practically at the same wavelength.

The complexation in dimethylformamide is apparently influenced by the strong nucleophilic properties of that solvent. This may be the reason for the formation of complexes with 1:1 molar ratio metal:ligand. Dimethylformamide ligands complete the saturation of the co-ordinative capacity of individual metal ions.

Attempts to study the complexation in pyridine were unsuccessful because of the strong absorption in the ultraviolet by that solvent.

Acknowledgment—The authors are grateful to the National Research Council (Ottawa, Ontario) for a grant that made this work possible.

B. W. BUDESINSKY*
J. SVEC

Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada

Summary—The composition and stabilities of hydrogen, manganese(II), iron(II), cobalt(II), nickel(II) and palladium(II) complexes with cyclopentadienide were investigated spectrophotometrically in aqueous and dimethylformamide solutions. Corresponding effective and overall stability constants were determined.

Zusammenfassung—Die Zusammensetzung und die Stabilität der Cyclopentadienidkomplexe von Wasserstoff, Mangan(II), Eisen(II), Kobalt(II), Nickel(II) und Palladium(II) wurden spektrophotometrisch an Lösungen in Wasser und in Dimethylformamid untersucht. Die entsprechenden effektiven und Gesamtstabilitätskonstanten wurden ermittelt.

Résumé—On a étudié spectrophotométriquement la composition et les stabilités des complexes de l'hydrogène, du manganèse(II), du fer(II), du cobalt(II), du nickel(II) et du palladium(II) avec le cyclopentadiénide en solution dans l'eau et le diméthylformamide. On a déterminé les constantes de stabilité effectives et globales correspondantes.

REFERENCES

1. M. L. H. Green in *Organometallic Compounds* (Edited by G. E. Coates, M. L. H. Green and K. Wade), Vol. 2 Methuen, London, 1968.
2. B. Raistrick, R. H. Sapiro and D. M. Newitt, *J. Chem. Soc.*, 1939, 1761.
3. B. W. Buděšínský, *Talanta*, 1969, **16**, 1277.
4. G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, 1944, **27**, 348.
5. B. W. Buděšínský, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1345.
6. B. W. Buděšínský and K. Haas, *Acta Chim. Acad. Sci. Hung.*, 1963, **39**, 7.
7. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*, 2nd Ed. Chem. Soc. Spec. Publ. 17, London, 1964.
8. R. E. Dessy, Y. Okuzumi and A. Chen, *J. Am. Chem. Soc.*, 1962, **84**, 2899.

---

* Present address: Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.

Talanta, 1972, Vol. 19, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Principles of Radiochemistry: H. A. C. McKay. Butterworths, London, 1971. Pp. 550. £13.00.

Written by a world-renowned chemist of long and vast experience, here is everything for all users of radioactivity as a tool. Origin, theories, handling, applications, everything is there with the exception of a cost analysis. At the price, this will inevitably be a book for the library, for reference, but perhaps two copies will be necessary—one for borrowing and one permanently on the shelves.

Treatise on Titrimetry; Volume 1, Inorganic Titrimetric Analysis (Contemporary Methods): Walter Wagner and Clarence J. Hull (edited by Joseph Jordan). Dekker, New York, 1971. Pp. xii + 225. $13.50.

It is fair comment on this compilation of methods to say that "contemporary titrimetry" ceased in 1968, or at least that is what appears to be the case. The only reference dated later than that not only has the year wrong but succeeds in transposing the digits in the volume number as well. The arrangement by groups of the periodic table is not as helpful or convenient as the general editor supposes, and an alphabetical arrangement would have been better. It is difficult to decide which is the more surprising in some of the choices of method—the ones that have been included or the ones that have been left out. According to the jacket of the book, advantages and limitations are pointed out; it is difficult, however, to see the advantage in recommending a method for copper that gives an error of 1–3% (pp. 13–14) when the "classical" version of the same reaction gives much lower error (a point made in the original of ref. 12 on p. 16 but omitted in the quotation from it). In short, this book is useful as a rough and ready guide to the literature up to late 1968 (for some journals—apparently earlier for others), but is limited by the selectivity imposed by the authors.

Analytical Methods for Atomic Absorption Spectrophotometry: edited by J. Kerber. Third Edition, Perkin–Elmer, Norwalk, Connecticut, 1971. $20.00.

This new edition of the well-known Perkin–Elmer manual replaces the 1968 edition, and will prove as generally useful as its predecessors. Like them, it carries the bonus of free supplements as they are issued.

Selected Annual Reviews of the Analytical Sciences, Volume 1: edited by L. S. Bark. Society for Analytical Chemistry, London, 1971. Pp. 269. £5.00; $12.50.

This first fruit of a new venture by the Society for Analytical Chemistry contains authoritative reviews on molecular-sieve chromatography, photoluminescence and chemiluminescence, activation analysis, atomic-absorption spectroscopy and catalytic methods. Those who regret the demise of the analytical section of the Annual Reports of the Chemical Society will find some consolation in these pages, although they will still mourn the loss of the comprehensiveness of the Reports.

Gas Chromatography: D. Ambrose. Second Edition, Butterworths, London, 1971. Pp. 321. £4.00, hard cover; £2.50, limp cover.

This revised edition of an already well-known work is to be welcomed for its thorough updating (up to 1970) of what is essentially a working chemist's guide to gas chromatography. Users of the first edition will know they should buy this one as well; newcomers will find it indispensable.

Nomenclature of Organic Chemistry: IUPAC. Third Edition, Butterworths, London, 1971. Pp. xiii + 337. £8.00.

The well-known "Sections A, B and C" of the IUPAC definitive rules on organic nomenclature have been revised and combined into a single handy volume, which will be welcomed by all organic chemists and all editors of chemical journals.

Problems in Advanced Organic Chemistry: Jerry March. Dekker, New York, 1971. Pp: viii + 421. $9.75.

These problems, ranging from bonding, through kinetics, mechanism and so on to literature searching, come complete with answers and will be a boon to those teachers who believe that the only way to learn to solve problems is to solve problems.

Oxidation: Techniques and Applications in Organic Synthesis, Vol. 2: R. L. AUGUSTINE and D. J. TRECKER. Dekker, New York, 1971. Pp. x + 204. $17.50.

This book contains review articles on four oxidation techniques in current vogue in organic chemistry, namely sulphoxide–carbodi-imide reactions, photo-oxygenation, hydrogen peroxide as reagent for producing epoxides, and metal ion–peroxide oxidations. Mechanism and application are both covered, and the volume should prove useful to the organic chemist interested in modern methods of synthesis.

Microtechniques—6: edited by G. KAINZ. Butterworths, London, 1971. Pp. 74. £2.00.

This volume contains the plenary lectures delivered at the IUPAC VIth Symposium on Microtechniques, organized by the Austrian Society for Microchemistry and Analytical Chemistry, in Graz in 1970. They cover inorganic and organic microanalysis, modern methods of organic structure determination, trace analysis by atomic-absorption and atomic-fluorescence spectroscopy, and modern radioanalytical methods.

Analytical Chemistry, Budapest 1970: edited by F. SZABADVÁRY. Butterworths, London, 1971. Pp. v + 201. £5.50.

This book contains the plenary lectures delivered at the IUPAC 3rd International Analytical Conference in Budapest, organized by the Hungarian Chemical Society and Academy of Sciences in 1970. The themes were solvent extraction of metal chelates, separation in inorganic and organic chemistry, a history of French analytical chemistry, electrolytic chromatography, enzyme electrode probes, chromic acid as oxidant in organic analysis, chromatographic polarography, pH, complexometric analysis, ion-exchange, ion-selective electrodes, reflectance spectroscopy, and thermal analysis.

Analytical Geochemistry: LORD ENERGLYN and L. BREALEY. Elsevier, Amsterdam, 1971. Pp. XV + 426. £9.25.

This is an account of the methods used today in geochemistry and geophysics, and the interests of its authors are reflected to some extent in the material chosen. Thus we are treated to a chapter on the principles of geochemistry as well as to the chemical methods of analysis used, and the sections on instrumentation occupy roughly half the book. In the purely chemical analysis sections, there are some surprising omissions, and some methods are simply reproduced from the literature quite uncritically. The English is rather quaint in places, and the proof-reader has left in "automatic sample spitter," presumably having taken this as a cry from the heart.

Conformational Analysis, Brussels, Belgium, 1969: edited by G. CHIURDOGLU. Butterworths, London, 1971. Pp. vi + 201. £5.30.

This volume contains the plenary lectures delivered at the IUPAC symposium on conformational analysis, organized in Belgium in 1969 by the Belgian Chemical Society, The Federation of Belgian Chemical Industries, and the University of Brussels, in 1969. The topics covered include the scope and limitations of the method, means of studying the conformation of compounds, and application of the technique to various systems.

Fluorescence Spectroscopy; An Introduction for Biology and Medicine: AMADEO J. PESCE, CARL-GUSTAF ROSÉN and TERRY L. PASBY. Dekker, New York, 1971. Pp. xiii + 247. $16.50.

This is a very readable account of fluorescence and should prove useful to others besides those readers indicated in the subtitle. There is the occasional lapse into the obscurity of jargon—for example, what is meant by "derivation of polarization of fluorescence equations"?— but the literature coverage is up to date (though selective) and the diagrams clear and helpful.

Flame Emission and Atomic Absorption Spectrometry; Volume 2—Components and Techniques: edited by JOHN A. DEAN and THEODORE C. RAINS. Dekker, New York, 1971. Pp. xiv + 362. $22.75.

As the title implies, this is essentially a practical guide to the equipment for flame spectroscopy, and how to use it. It is therefore packed with useful information, and likely to prove a flame-spectroscopists *vade mecum*.

Talanta, 1972, Vol. 19, pp. 93 to 124. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

ORGANIC ANALYSIS BY LUMINESCENCE METHODS

J. Bartos and M. Pesez
Centre de Recherches Roussel-Uclaf, F.93-Romainville, France

(*Received* 17 *March* 1971. *Accepted* 27 *July* 1971)

Summary—This review presents the major features of luminescence methods relating to the estimation of organic compounds in solution. A notation for reporting fluorimetric determinations is proposed. The outstanding factors affecting the fluorescence of solutions are briefly reviewed, and determinations of compounds offering a native fluorescence are illustrated by selected examples. Special attention is paid to functional fluorimetry and to the determination of non-fluorescent compounds by means of chemical reactions giving rise to fluorescent species. Some enzymatic reactions are described, as far as they allow the estimation of definite chemicals. Phosphorimetry and chemiluminescence are exemplified. An appendix presents some new functional fluorimetric determinations developed by the authors.

From 1957 to 1965, some 2000 papers were published on fluorimetric analysis, and the last biennial review in *Analytical Chemistry*,[1] covering the period approximately from December 1967 to December 1969, contains 763 references. Even if it is taken into account that these references include inorganic chemistry, it is obvious that an exhaustive bibliography of studies dealing with organic analysis by luminescence methods could not be condensed within the pages allocated to this review, and would duplicate existing reviews. Moreover, various books and monographs have been issued these last five years, trying to keep the analyst's knowledge in this field up to date.[2-9]

This review is limited to the presentation of the features of luminescence methods relating to the estimation of organic compounds in solution, and its major part is obviously devoted to fluorimetry. A notation for reporting determinations is suggested which will facilitate comparisons between results obtained with different apparatus. The outstanding factors affecting the fluorescence of solutions are reviewed, and determinations of compounds offering a native fluorescence are illustrated by some selected examples. Particular emphasis is placed on estimations which involve chemical reactions: functional fluorimetry and determinations of definite compounds. One section deals with some enzymatic reactions. Phosphorimetry and chemiluminescence, which have been scarcely applied until now to the determination of organic compounds are briefly dealt with. Theories of luminescence methods, and instrumentation are not dealt with, these topics being already widely covered.[2-4,9]

FLUORIMETRY

Fluorescence is the emission of light from a molecule which returns to its normal ground state from the lowest vibrational level of an excited singlet state, the excitation being achieved by the absorption of light.

---

* For reprints see Publisher's announcement at end of issue.

When compared to absorptiometric methods, fluorimetry offers various advantages. The sensitivity is usually from 10- to 100-fold greater, and in many instances allows work at levels below 1 ppm. Fluorescence methods may be specific. Only a limited number of molecules fluoresce, and they have individual excitation and emission spectra. With selected excitation and emission wavelengths, it is possible to determine a fluorescent compound in mixtures without tedious separations. Slightly turbid or coloured solutions do not generally lead to serious interferences.

On the other hand, the intensities of the fluorescence spectra are proportional to the concentration of the species only in dilute solutions. At higher concentrations, the intensity falls off, owing to inner-filter effects. Determinations must therefore be limited to the range over which linearity is observed. Commercially available instruments do not allow one to obtain an absolute expression of the fluorescence intensity, analogous to absorbance, and the excitation and emission spectra recorded with the usual spectrofluorimeters are distorted. However, in order to determine the concentration of a compound in solution, it is not necessary to know the relationship between uncorrected and true spectra, since at given excitation and emission wavelengths, the correction coefficient is the same for the sample, the blank and the reference.

Reporting results

In reports of determinations problems arise from the lack of an absolute expression of the fluorescence intensity and from the fact that the blank almost always fluoresces, particularly when a chemical reaction is involved. Most spectrofluorimeters are equipped with a zero potentiometer which is utilized to set the meter at zero and to supply blank suppression, but the deflection given by the sample remains arbitrary, varying with the adjustments.

Different methods are used to overcome these problems, and standardization would be highly desirable in this field, permitting a ready comparison of results gathered by authors working with various apparatus.

The instrument can simply be adjusted to read 50 per cent of full scale for a given concentration of the compound to be determined.[10] The fluorescence intensities of the samples can also be expressed in terms of an intensity scale on which a standard solution gives a deflection of 100 meter divisions, at the same wavelengths of excitation and emission.[11] Standard solutions of quinine sulphate, sodium fluoresceinate or 2-aminopyridine have often been used. With these methods, the blank value is not taken into account, and it is worth knowing it, since impurities are of the highest importance in fluorimetric determinations. The blank can vary widely from one series of assays to another, even with analytical-grade solvents and reagents.

Some authors give the limits of the range over which a linear relationship between concentration and emission of light is observed, and they express the blank value in μg/ml of the compound to be determined.[12,13] When concentrations are plotted on the x axis and readings on the y axis, this equivalent is the abscissa of the point where the extrapolated straight line for concentration *vs.* reading reaches the x axis.

In our first paper on fluorimetric functional analysis,[14] we proposed another notation. The meter is set at zero with the photomultiplier shutter closed. We give two limit values for the determination, the upper corresponding to a deflection of 100 meter units, the lower to the smallest weight of compound which can be estimated with a reasonable accuracy. It is of course implied that the relationship of concentration to reading is linear over this range. We also report the sample weight and the concentration of a suitable standard both corresponding to a deflection of 50 units. Therefore, knowing the sample concentrations which give readings 100 and 50, and since linearity is observed, it is easy to calculate the blank deflection. On the other hand, the knowledge of the standard concentration corresponding to the deflection 50 permits the proper adjustment of any fluorimeter. It must be verified that the cells used do not afford a noticeable interfering fluorescence. If they do, the corresponding readings must be subtracted from the respective deflections given by the blank, the samples and the standard.

Comparison of results obtained with two instruments (Farrand equipped with xenon lamp and gratings, and Electrosynthèse* with low-pressure mercury lamp and filters) showed only very slight discrepancies, probably due to the widths of the spectral bands. Therefore, the numerical values given make our results readily reproducible with other instruments, and it also becomes easy to find out whether unexpected discrepancies are related to an abnormal fluorescence of the blank, caused by the solvents or reagents. We suggest this method for reporting results be adopted by analysts dealing with fluorimetric determinations in solution.

It must be pointed out that it is not always worth operating at the wavelengths corresponding to the most intense emission of light from the sample, but at those corresponding to the highest difference between sample and blank. In our procedures, whenever possible, we propose an excitation wavelength accessible to apparatus equipped with a low-pressure mercury lamp and glass cells, *i.e.*, 366, 405, 436 and 546 nm, so that our results can be reproduced even with very simple instrumentation. The study of excitation and emission spectra recorded on a Farrand spectrofluorimeter has shown that, in these instances, the selection of the true optimum excitation wavelength would multiply the sensitivity only by a coefficient lower than 2.

It must also be emphasized that, when chemical reactions are involved in fluorimetric estimations in solution, the lower limit of the determination is strictly dependent upon the blank fluorescence, which cannot be avoided. Even if the fluorescent species would allow determination at a level of, *e.g.*, 10 ng, the blank may afford a fluorescence intensity corresponding to, *e.g.*, 1 μg of the said species, and therefore accurate determinations become possible only at levels permitting an appreciable difference between the assay and blank signals.

Factors affecting the fluorescence of solutions

The main factors affecting the fluorescence of a compound in solution at concentrations usually used for determinations are: solvent, pH, oxygen, photodecomposition, temperature. These effects have already been described and discussed in various books and reviews,[2,4,6,15] and we have gathered here only some information exemplifying them.

Solvent effects. In many instances, for a given compound, the colour and intensity of fluorescence vary with the nature of the solvent. The interpretation of these effects is often complicated, because the observed changes may be the resultant of several quite different forces which may either reinforce or minimize each other. Some of these phenomena are still imperfectly understood.

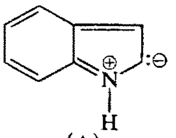
Changes in emission spectra may or may not be accompanied by modifications in the excitation spectrum. Changes in both spectra imply interaction with solvent in

---

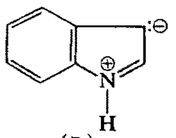
* Manufactured in France.

both ground and excited states of the molecule. Changes in only the emission spectrum mean that there is an interaction between solvent and the excited state of the molecule, but the ground state is not involved.

Provided that hydrogen-bonding does not take place, the effect of the solvent can often be related to its dielectric constant. Indole and substituted indoles show pronounced shifts to longer wavelengths in their fluorescence emission maxima with increasing dielectric constant of the solvent,[16] but comparable shifts are not observed in the fluorescence excitation spectrum. Polar mesomeric forms of indole such as (A) and (B) may make a larger contribution in the excited state of indole than in the ground state and such structures are expected to be more sensitive to the dielectric constant of the surrounding solvents. This explains why changes occur in emission spectra only.



(A)



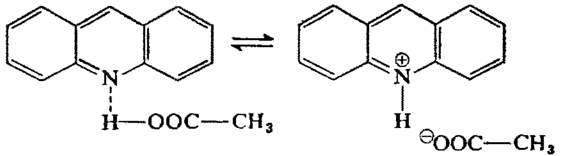
(B)

The quantum yield of dansyl DL-tryptophan increases with decreasing dielectric constant of the solvent: 0·068 in water, 0·35 in acetone and 0·70 in dioxan. At the same time, the fluorescence emission maximum shifts towards shorter wavelengths: 578, 513 and 500 nm respectively.[17]

In some instances, the refractive index of the solvent plays a role. In non-polar media, the shift of the fluorescence maximum of 1- and 2-acetylanthracenes increases with increasing refractive index of the medium.[18]

The viscosity of the solvent must also be taken into account. It is well known that increase in molecular rigidity and co-planarity of the rings increase fluorescence efficiency. It may thus be expected that substances possessing substituted phenyl groups which are capable of internal rotation will increase their fluorescence when dissolved in a medium which will rigidify them. For example, a diphenylmethane dye such as Auramine O becomes fluorescent when dissolved in a viscous medium (*e.g.*, glycerol).[19] Incidentally, it was found that this effect provides an extremely convenient means for measuring the viscosity of high-viscosity media.

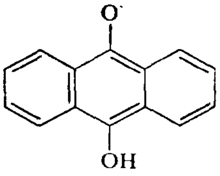
A compound may form hydrogen bonds with solvents in both the ground and excited states. In non-polar solvents such as benzene, chlorophyll shows only a weak fluorescence when water is rigorously excluded.[20] Addition of water or of a polar solvent causes a remarkable enhancement of fluorescence, due to hydrogen-bonding between the solvent and chlorophyll. The fluorescence of acridine in benzene solutions increases on addition of acetic acid,[21] and there are only minor changes in absorption. The hydrogen bond formation takes place in the ground state (C), but in the excited state an ion-pair (D) predominates, *i.e.*, in the excited state the equilibrium is shifted to the right as a result of the increased basicity.



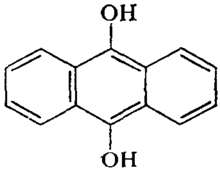
(C) (D)

Fluorescence quenching by solvent may permit selective determinations (see below under native fluorescence). Quenching processes divert the absorbed energy into channels other than fluorescence.

In its excited state, a molecule may react with the solvent. In alcohol solution, the singlet excited state of anthraquinone goes to the triplet state, which reacts with alcohol to form the semiquinone radical (E) and the alcohol radical which further reacts with a ground-state anthraquinone molecule to produce a second semiquinone radical and one aldehyde molecule. Through a disproportionation reaction, two semiquinone radicals give one molecule of anthraquinone and one molecule of 9,10-dihydroxyanthracene (F), which is highly fluorescent. Oxygen traps the radical (E), and the fluorescence is observed only in its absence.[22,23]



(E)



(F)

pH effects. It is obvious that for a compound which can undergo ionization, the neutral species, the anion and the cation may be differently excited, leading to different excitation and emission spectra. For example, the dibasic ion of quinine fluoresces blue, the monobasic ion fluoresces violet and the undissociated base does not fluoresce at all.

Compounds may be more acidic or more basic in the excited state than in the ground state. In acidic dimethylformamide, 8-aminofluoranthene absorbs as the cation and emits as the neutral amine. The deprotonation has taken place owing to collisions within the duration of excitation.[6] A methanol–trifluoroacetic acid solution of 9-acridanone shows the excitation spectrum of the neutral species and the emission spectrum of the cation. In strongly alkaline solution, the excitation and emission spectra are both derived from the anion.[24]

We shall not extend this paragraph beyond these examples, since a detailed study of pH effects has been given in a previous *Talanta* review.[6] Moreover, an account has been given recently of the theory of the effect of pH change on fluorescence of organic species which exhibit acid-base properties, and of the practical application of this effect.[25]

Effect of oxygen. Oxygen may decrease the fluorescence intensity of a compound by oxidizing it, and this reaction may be catalysed by ultraviolet irradiation. It may also accelerate the photodecomposition of the fluorescent species.[26] But often there is neither chemical decomposition nor catalysis of photodecomposition, and yet the fluorescence of almost all organic compounds is quenched at least slightly by oxygen. It is believed that, generally, the quenching is caused by a reaction between oxygen and the excited singlet state of the molecule, giving rise to a triplet state.[27]

Photodecomposition. Substances sensitive to ultraviolet light may of course suffer a photodecomposition during a prolonged fluorimetric examination. Reasonably rapid measurements are recommended in order to overcome this problem, particularly with very dilute solutions.

Temperature effects. Fluorescence intensity usually decreases with increasing temperature, owing to higher probabilities for the other means of deactivation of the excited molecule. Since most fluorimetric measurements are made at room temperature, it is best to take this temperature into account and to obviate heating of the sample chamber by excitation light, by using a suitable thermostatic arrangement whenever necessary.

Compounds possessing native fluorescence

De Ment[28] listed about 3000 compounds possessing native fluorescence. Some 600 are purely organic and fluoresce in solution. They can of course be determined without any prior reaction, usually at levels of 0·1–1·0 μg/ml, sometimes at much lower concentrations (*e.g.*, 0·1 ng/ml for quinine sulphate). Modern spectrofluorimeters permit detection and measurement of ultraviolet fluorescence, thus extending the field of these determinations. Suitable selection of pH, wavelength combinations and solvents are of the highest importance, and this section is limited to some selected examples pointing out these outstanding features.

Some phenols have been determined recently.[29] With one exception, they fluoresce in the ultraviolet region and, for each species, an optimum pH was proposed: phenol, excitation 276 nm, emission 365 nm, pyrocatechol 282/345 nm, hydroquinone, 298/350 nm, in 0·010–0·011M sulphuric acid; 4-hydroxybenzoic acid, 290/355 nm, in 0·10M sodium hydroxide; gentisic acid, 328/459 nm, in pH 5·5 buffer; protocatechuic acid, 300/370 nm, in pH 8·9 buffer.

Mixtures of 2- and 3-hydroxybenzoic acids can be analysed. At pH 12·0, both isomers fluoresce, whereas at pH 5·5 only the 2-isomer is fluorescent. 4-Hydroxybenzoic acid does not fluoresce at these two pH values and does not interfere.[30]

When excited at 295 nm, a neutral solution of serotonin exhibits an emission-peak at 330 nm. In acidic medium, this peak fades and another appears at 550 nm, reaching its maximum value in 3N hydrochloric acid.[31] An acid may intervene not only through its hydrogen ion, but also through its anion. For example, fluorescence of quinine sulphate is usually measured in 0·1N sulphuric acid. No fluorescence is observed in 0·1M hydrochloric acid. The fluorescences of fluorescein and Rhodamine are strongly diminished if the solutions contain a few per cent of salts such as potassium iodide or sodium chloride. Iodide ion also quenches the fluorescence of vitamin B_2.

Formaldehyde and acrolein both react with J-acid in sulphuric acid, yielding fluorescent chromogens which emit in the 500-nm region. Upon addition of water, the formaldehyde chromogen becomes virtually non-fluorescent at this wavelength.[32]

A suitable selection of excitation and emission wavelengths allows the determination of salicylic and acetylsalicylic acids in aspirin tablets.[33] The solvent is 1% acetic acid in chloroform. Salicylic acid is estimated at 308/450 nm, and acetylsalicylic acid at 280/335 nm, after a further dilution with the same solvent.

At the same excitation wavelength (365 nm), 1-naphthol and 2-naphthol in 0·2M sodium hydroxide were determined at emissions 480 nm and 426 nm respectively.[34]

A striking example of suitable selection of pH, wavelengths and solvent is given by the analysis of mixtures of morphine, codeine, narcotine and papaverine, the principal opium alkaloids.[11] A sample is dissolved in 0·1N sulphuric acid and most of the narcotine and papaverine are stripped from the acidic solution with chloroform. In the acidic medium, morphine and codeine both exhibit almost similar fluorescences.

In 0·1*M* sodium hydroxide, the fluorescence of codeine is only about 10% less intense than in 0·1*N* sulphuric acid, whereas that of morphine strongly weakens. Thus, a differential method allows the determination of these two species. Papaverine and narcotine are quantitatively extracted from a pH 9 buffer solution into chloroform. Papaverine fluorescence is measured at 320/348 nm. Narcotine does not interfere (maxima 335/400 nm). The addition of trichloroacetic acid to the chloroform solution intensifies the fluorescence of narcotine and shifts the maxima to 315/375 nm, whereas the fluorescence of papaverine is depressed and its maxima are shifted to 417/455 nm, thereby causing no interference in narcotine determination.

Quenchofluorimetric analysis[35] was applied to the selective estimation of various polynuclear compounds. For instance, in *o*-cresol solution, most of the aromatic amines remain fluorescent, whereas aza heterocyclic hydrocarbons and most of the heterocyclic imines are quenched. Nitromethane quenches the fluorescence of aromatic amines, heterocyclic imines, and most aromatic hydrocarbons except those containing a fluoranthene ring. With nitrogen dioxide–trifluoroacetic acid as the solvent, aza heterocyclic hydrocarbons remain fluorescent, aromatic amines, heterocyclic imines and polycyclic aromatic hydrocarbons are quenched.[36] A more detailed study of air pollutants was the subject of a previous *Talanta* review.[6]

A chemical reaction can also quench the fluorescence of one of the components of a mixture. For example, the Diels–Alder reaction of maleic anhydride with anthracene removes the lowest energy electronic transition of this hydrocarbon, permitting the fluorimetric measurement of pyrene, diphenylstilbene and perylene in the presence of the adduct.[37]

Raman effect. In determination of compounds possessing native fluorescence, with modern sensitive spectrofluorimeters, the limit of sensitivity is set by the magnitude of the blank. Some interferences can be avoided by choosing proper material for the cells, using efficient monochromators, high-purity solvents, *etc.* But in operations at high sensitivities, Raman emission from the solvent cannot be overcome.[38] For instance, when a solution of quinine sulphate in 0·1*N* sulphuric acid is excited at 365 nm, the main Raman band of water occurs at 416 nm and overlaps the edge of the fluorescence spectrum of the sample. At a dilution of 1 ng/ml, this band may be mistaken for part of the structure of the quinine sulphate band. The emission spectrum of a very dilute anthracene solution in *cyclo*hexane appears to have an additional band. Excitation spectra are also distorted, and these interferences can be even more important with filter fluorimeters.

All solvents containing hydrogen atoms interfere, and carbon tetrachloride is the most satisfactory solvent for high sensitivity spectrofluorimetry. The band shown by chloroform is less intense than those of water, ethanol or *cyclo*hexane. Raman bands are readily identified, since there is a constant difference between the wavenumber of the exciting light and the wavenumber of the Raman band.

For instance, with the excitation monochromator set at 365 nm, the wavelength of the main Raman band produced by water is 416 nm. With excitation at 405 nm, this band is shifted to 469 nm.

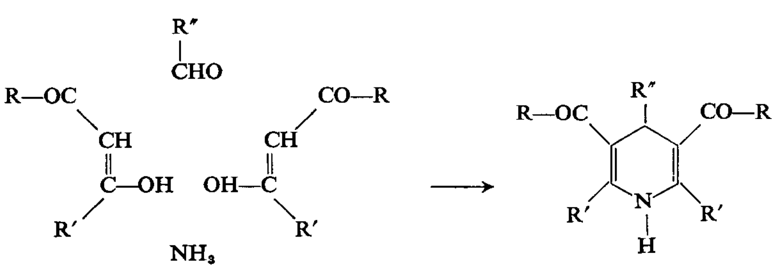
Functional organic fluorimetry

This branch of fluorimetry is based on chemical reactions characteristic of the various functional groups. A given reaction may therefore be applied to different molecules bearing the same group. Widely used in colorimetry for many years, this approach had until 1967 been but scarcely applied to fluorimetric determinations, probably because it is much easier to predict the development of a colour than of a fluorescence. But the knowledge of the compounds already described as being fluorescent, the study of their methods of preparation and the replacement, in the course of the synthesis, of one of the components by another molecule bearing the same functional group, recently led to an appreciable extension of this field of analysis. Furthermore, some unreactive groups can be converted into more reactive ones, or a molecule can be degraded, yielding a reactive species.

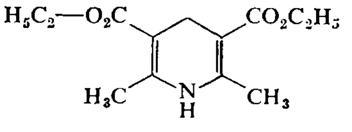
The following table summarizes the main references relative to the functional group determinations mentioned in this section.

Alcohols;[61] primary;[40] primary, α-amino-;[13,14] primary, 2-nitro-;[14] 1,2-diols[13,14]
Aldehydes, aliphatic;[13,14] α-methylenic-[66]
Alkylamines, primary, secondary and tertiary;[44] primary and secondary,[39,48] (appendix);[14,43] primary, (appendix); tertiary[39]
Arylamines, primary (appendix)
Carboxylic acids, α-amino-;[39,48] 2,3-dihydroxy-;[14] α-oxo-[77,78]
Dibenzazepine derivatives[84]
Ethylenic compounds, $R—CH=CH_2$[13,14]
Guanidines, monosubstituted and *N*,*N*-disubstituted;[50,51] monosubstituted (appendix)
Hexitols[13,14]
Hexuronic acids[14]
Indoles[39,81]
Ketones;[76] α-methylenic dialkyl-;[49] α-diketones[78]
Nitriles[14]
Phenols[14]
Phenothiazine derivatives[82,83]
gem-Polyhalogen derivatives[79]
Pyridine derivatives[80]
Steroids, Δ^4 and $\Delta^{1,4}$-3,11-dioxo;[39] guanylhydrazones;[91] hydroxy-;[61] 17-ketol-;[13,14] $\Delta^{5(10)}$-3-oxo-19-nor-[39]
Sugars: aldohexoses;[10,87,88] aldoses;[86] 2-amino-sugars;[90] carbohydrates;[85] 2-deoxyoses;[14] ketoses (appendix); pentoses[39]
Thiols[62,63]
Thioureas, *N*,*N'*-disubstituted[55]
Ureas, monosubstituted and *N*,*N'*-disubstituted.[55]

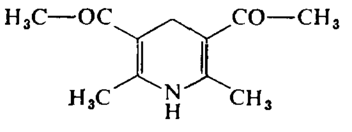
Dihydropyridine derivatives are formed through the Hantzsch reaction, by condensing two molecules of a β-keto ester or a β-diketone with one molecule each of aldehyde and ammonia:



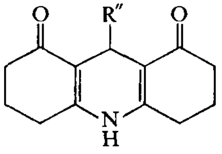
Derivatives obtained from ethyl acetoacetate (I), 2,4-pentanedione (II), 1,3-*cyclo*hexanedione (III) and dimedone (IV) are fluorescent.



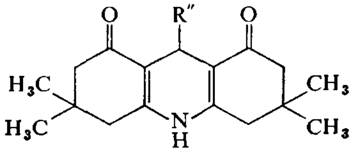
(I)



(II)



(III)



(IV)

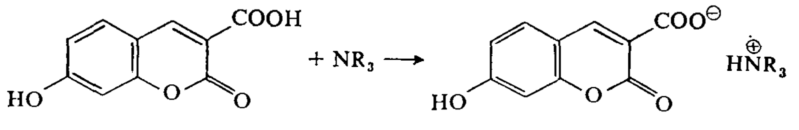
Thus, a mixture of ammonium acetate with ethylaceto acetate,[14] 2,4-pentanedione[13] or dimedone[13] allows the determination of formaldehyde, and hence of compounds which afford formaldehyde by suitable chemical reactions: 1,2-diols, hexitols, primary α-aminoalcohols, and 17-ketolsteroids oxidized with periodate ion,[13,14] ethylenic compounds of formula R—CH=CH_2 oxidized with a mixture of permanganate and periodate ions,[13,14] and aliphatic 2-nitro-1-hydroxy compounds decomposed in alkaline medium.[14]

The ethyl acetoacetate and 2,4-pentanedione methods are the most specific for formaldehyde, whereas the estimation of other aliphatic aldehydes is achieved with dimedone[12] or *cyclo*hexanedione.[12,14] The last reagent was also used for the determination of pentoses, after their dehydration into furfural,[39] and of primary alcohols,[40] oxidized to aldehydes with 2,6-dichloro-4-trimethylammonium phenyldiazonium ion.[41,42]

J-Acid (6-amino-1-naphthol-3-sulphonic acid) was also proposed for the estimation of formaldehyde obtained by oxidative degradations.[13] The fluorescent chromogen formed is a dibenzoxanthylium derivative.[32]

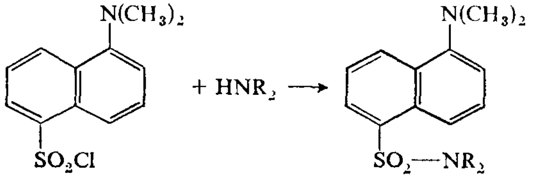
The Hantzsch reaction also allows the determination of primary alkylamines, α-amino acids[14,39,43] and nitriles, which are reduced to primary alkylamines by potassium borohydride in alkaline medium containing palladium.[14] The reagent is an aqueous solution of 2,4-pentanedione and formaldehyde.

Various other fluorimetric methods have been described for nitrogenous bases. The reaction of primary, secondary and tertiary aliphatic, and secondary and tertiary cyclic amines with 3-carboxy-7-hydroxycoumarin results in an increase in fluorescence, accompanied by a change in the activation wavelength of the mixture, permitting the measurement of the reaction product even in the presence of an excess of fluorescent coumarin reagent.[44]

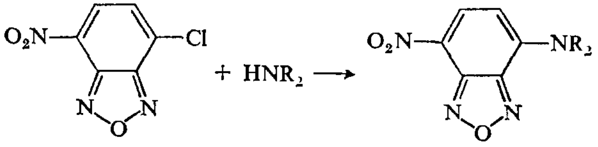


Aromatic amines and aromatic heterocycles do not react.

Dansyl chloride (1-dimethylaminonaphthalene-5-sulphonyl chloride) has been widely used in peptide and amino-acid studies,[45] and in fluorimetric estimation of amines after separation by thin-layer chromatography.[46] In non-aqueous medium, the chloride is much less fluorescent than the sulphonamide, thus allowing fluorimetric determination of primary and secondary alkylamines without any previous separation of the excess of reagent.[39]



4-Chloro-7-nitrobenzofurazan (identical with 7-chloro-4-nitrobenzofurazan or 4-chloro-7-nitro-2,1,3-benzoxadiazole) has been proposed for the determination of amines and amino-acids.[47]

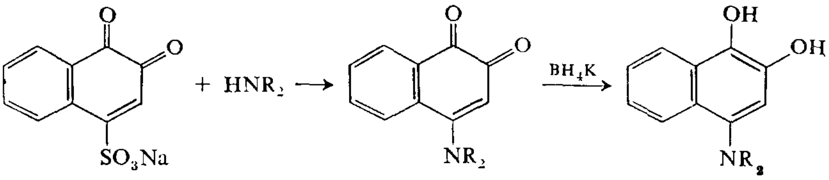


In ethanolic solution, it allows the determination of primary and secondary alkylamines (see Appendix). Amino-acids also react, but there is no linear relationship between concentration and light emission.

o-Diacetylbenzene, already used for colour and fluorescence detection of amines, amino-acids and proteins, also permits a sensitive fluorimetric estimation of primary alkylamines (see Appendix). The mechanism of this reaction is unknown.

A colour test has been proposed for the detection of tertiary alkylamines, using a solution of α,γ-anhydroaconitic acid in acetic anhydride. Under suitable conditions, the same reagent permits the fluorimetric determination of these amines.[39]

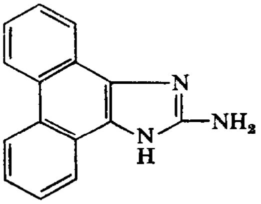
The dye obtained by reacting primary and secondary alkylamines with 1,2-naphthoquinone-4-sulphonic acid is extractable into methylene chloride. Reduction by potassium borohydride yields a fluorescent *o*-diphenol, allowing the fluorimetric estimation of these nitrogenous bases.[48]



Primary arylamines have also been determined, using a somewhat different procedure (see Appendix) which gave negative results with alkylamines. The same reagent allows the fluorimetric estimation of α-methylenic dialkylketones.[49]

In alkaline solution, ninhydrin is converted into *o*-carboxyphenylglyoxal which can give rise to fluorescent Schiff's bases with the free NH_2-group of guanidine or monosubstituted and *N,N*-disubstituted guanidines, permitting their fluorimetric determination.[50,51] The reaction has been applied to the determination of dihydrostreptomycin.[52]

Phenanthrenequinone has been proposed as an analytical reagent for arginine and other monosubstituted guanidines.[53] According to the authors, arginine, guanidine, methylguanidine and *p*-tosylarginine yield, upon reaction with this quinone, the same fluorescent species, identified as 2-amino-1*H*-phenanthro-[9,10-*d*]-imidazole-(V). The mechanism of this reaction as yet is unknown.

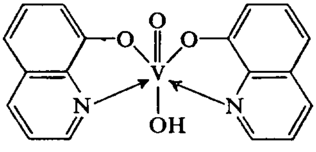


(V)

Under suitable conditions, there is a linear relationship between the concentration of a monosubstituted guanidine and light emission, which permits the fluorimetric determination of this class of compounds (see Appendix).

Although, as a general rule, fluorescence is quenched by nitro groups, one of us has shown that picric acid, on reaction with *N,N'*-dicyclohexylcarbodiimide or *N,N'*-dibenzylcarbodi-imide gives fluorescent guanylisoureas.[54] An excess of picric acid unfortunately quenches the fluorescence. When other aromatic trinitro derivatives were tested, it was found that 2,4,6-trinitrobenzoic acid also formed, with these carbodi-imides, a yellow fluorescent adduct, the structure of which has not yet been established. An excess of reagent did not interfere. Carbodi-imides are obtained by treating ureas with *p*-toluenesulphonyl chloride in pyridine, or thioureas with mercuric oxide. These reactions thus allow fluorimetric determination of urea, monosubstituted and *N,N'*-disubstituted ureas, and *N,N'*-disubstituted thioureas.[55] Derivatives with aromatic substituents do not react.

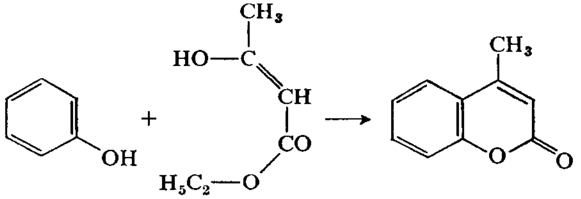
The blue-violet solution of di-(8-hydroxyquinolyl)orthovanadic acid (VI) in chloroform turns to red on addition of an alcohol. The excess of reagent is stripped



(VI)

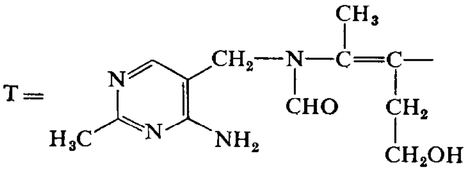
from the organic phase with an aqueous solution of sodium hydroxide, in which the red species, the structure of which is not known with certainty,[56–59] is insoluble.[60] This red form is then hydrolysed by adding hydrochloric acid to the organic phase, and the liberated 8-hydroxyquinoline, reacting with magnesium ion, yields a fluorescent complex. Primary, secondary and tertiary alcohols, as well as hydroxysteroids, are so determined.[61]

Fluorimetric determination of phenols is achieved by converting them into coumarins, with ethyl acetoacetate in sulphuric acid medium.[14]



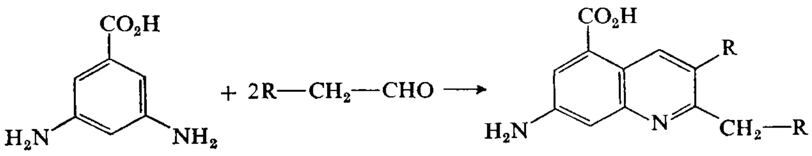
An exchange reaction occurs between symmetric thiamine disulphide and the —SH group of thiols. The liberated thiamine sulphide is oxidized to fluorescent thiochrome by ferricyanide in alkaline medium.[62,63] The following equations have been proposed:

$$\mathrm{R{-}SH + T{-}S{-}S{-}T \rightarrow R{-}S{-}S{-}T + T{-}SH}$$
$$\mathrm{2R{-}SH + T{-}S{-}S{-}T \rightarrow R{-}S{-}S{-}R + 2T{-}SH}$$



There is a linear relationship between the intensity of the fluorescence emitted by the thiochrome and the original concentration the thiol.

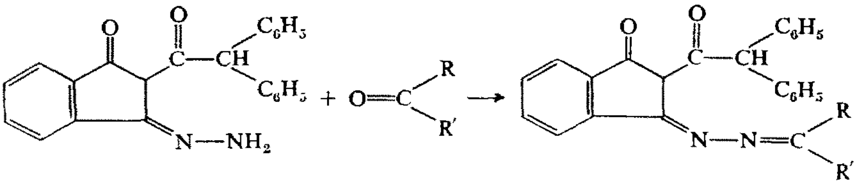
Through the Doebner–Miller synthesis for quinolines, aldehydes with an α-methylene group, reacting with 3,5-diaminobenzoic acid in acidic medium, afford a fluorescent 2,3-dialkyl-5-carboxy-7-aminoquinoline.



[For the mechanism of the reaction, see Refs. 64, 65]

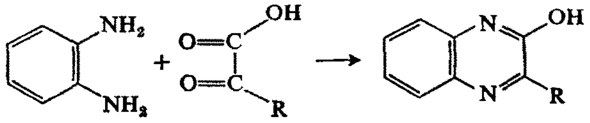
This method allows the determination of α-methylene aldehydes[66] and 2-desoxy-sugars.[14] It has been applied to the determination of acetaldehyde obtained by enzymatic decarboxylation of pyruvic acid,[67] of succinic semialdehyde produced from γ-aminobutyrate during incubation with a transaminase,[68] of deoxyribonucleic acid,[69,70] 2-deoxyglucose[71,72] and sialic acid,[73] which yields a 2-deoxy-4-aminooctose upon deacetylation and decarboxylation.

2-Diphenylacetyl-1,3-indandione-1-hydrazone was introduced in 1958 as a useful reagent for characterizing carbonyl compounds.[74]

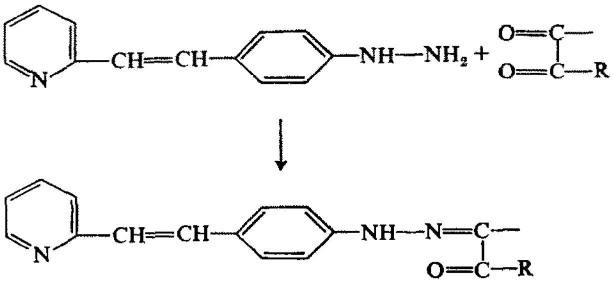


The fluorescent azine allowed the detection of acetone,[75] and was applied to the spectrofluorimetric determination of carbonyl compounds.[76] Unfortunately, the reagent itself strongly fluoresces in the same regions as the azine derivatives, and estimations are possible only after a chromatographic separation.

α-Oxo-acids give fluorescent hydroxyquinoxaline derivatives when condensed with *o*-phenylenediamine in sulphuric acid medium:[77]

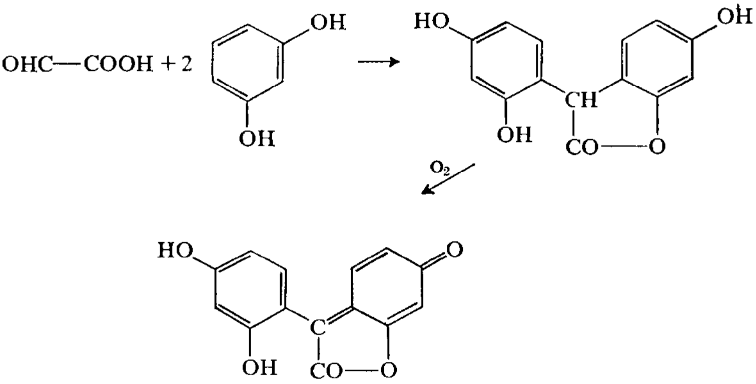


They also react with 4′-hydrazino-2-stilbazole, which is selective for α-oxo acids and α-diketones:[78]

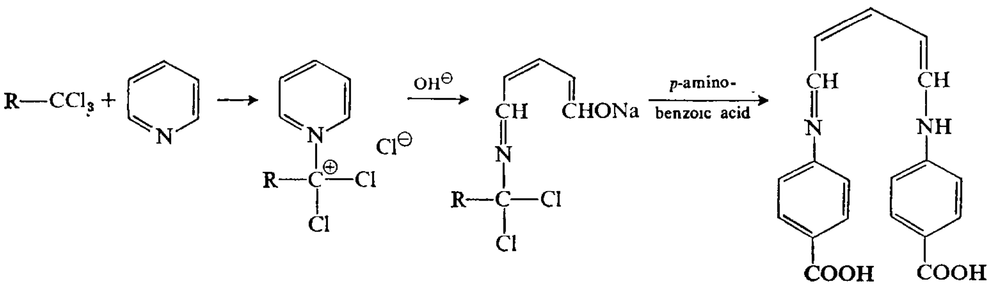


The reagent itself, and the hydrazones of monocarbonyl compounds such as acetone strongly fluoresce at pH 7–12, whereas those of α-oxo-acids and α-diketones fluoresce at pH lower than 2.

2,3-Dihydroxycarboxylic acids, such as tartaric acid, and hexuronic acids can be oxidized to glyoxylic acid which in acidic medium condenses with resorcinol, and the resultant lactone is oxidized in air to a fluorescent dye:[14]



According to the Fujiwara reaction, *gem*-polyhalogen compounds open up the pyridine ring to give a glutaconic dialdehyde derivative. This reacts with *p*-aminobenzoic acid, yielding a fluorescent Schiff's base, allowing the fluorimetry of the *gem*-polyhalogen derivatives.[79]



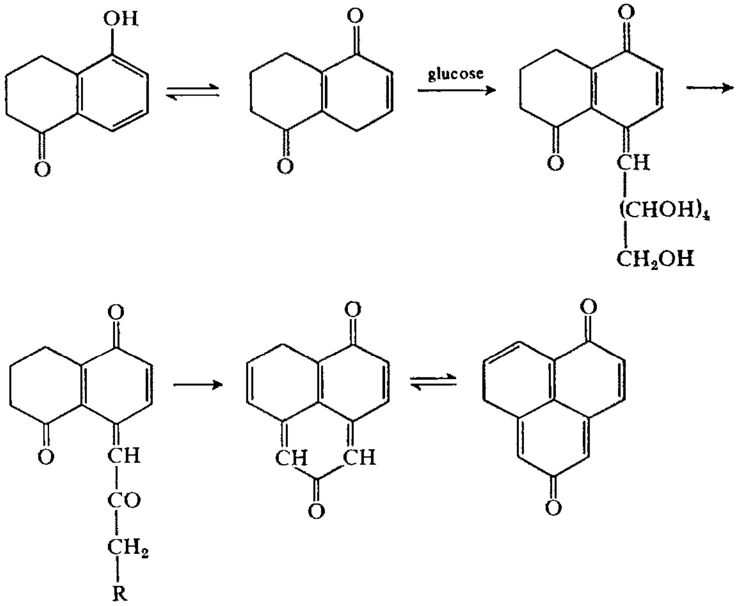
The pyridine ring is also opened up by cyanogen bromide. A further reaction with *p*-aminobenzoic acid thus permits the fluorimetric determination of pyridine derivatives.[80] 4-Hydroxypyridine and α-substituted derivatives do not react.

Upon condensing them with formaldehyde in the presence of an oxidizing agent, indole compounds develop a fluorescence.[39] The mechanism of this reaction is unknown. Some 3- and 5-substituted indoles were also determined with *o*-phthalaldehyde.[81]

Phenothiazine derivatives offer a native fluorescence. It is modified, and greatly increased, under the action of oxidizing agents such as potassium permanganate or hydrogen peroxide, thus allowing measurements in the submicrogram range.[82,83] Permanganate oxidation also permits the fluorimetric estimation of dibenz[*b,f*]-azepine derivatives.[84]

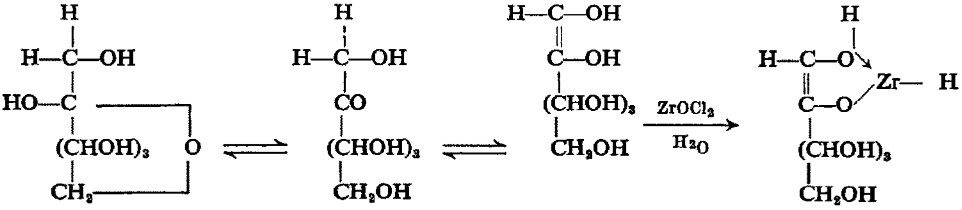
A variety of carbohydrates react with *o*-phenylenediamine to form fluorescent derivatives, which allow their determination.[85] The mechanisms of the reactions involved are still being discussed.

Aldoses are dehydrated in hydrochloric acid medium, and then condensed with resorcinol to yield presumably xanthenone derivatives.[86] The fluorescence is green for pentoses, blue for hexoses. Hexoses react with 5-hydroxytetralone, forming benzonaphthenone which permits their determination by fluorimetry.[10,87,88] The following mechanism has been proposed:



The step in which three carbon atoms from the hexose unit are eliminated is not explained.

Ketoses form a fluorescent adduct with zirconyl chloride[89]:

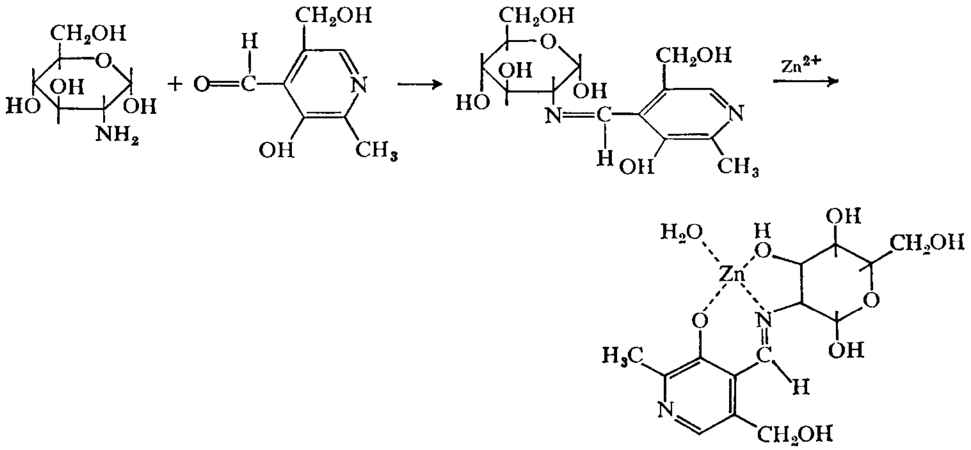


Under suitable conditions, the fluorimetric determination of these carbohydrates becomes possible (see Appendix). Aldopentoses and aldohexoses react but weakly.

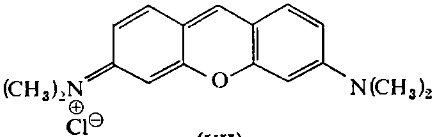
2-Amino-sugars reacting with pyridoxal and zinc ions form a fluorescent zinc chelate of pyridoxylideneamino-sugar containing a 1:1 ratio of amino-sugar to zinc.[90] (See p. 108.)

Steroid guanylhydrazones yield fluorescent derivatives upon reaction with phenanthrenequinone in alkaline medium.[91] Δ^4- and $\Delta^{1,4}$-3,11-dioxosteroids give fluorescent adducts, of unknown structure, with 2,6-di-t-butyl-*p*-cresol.[39]

It was shown that, under the action of $\Delta^{5(10)}$-3-oxo-19-norsteroids in alkaline medium, the colour of thionine or Methylene Blue rapidly changes. Under similar conditions, the fluorescence of Pyronine G (VII), the structure of which may be



compared to that of Methylene Blue, rapidly decreases, thus allowing the determination of this class of steroids by the decrease in fluorescence.[39]



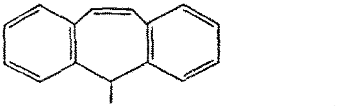
(VII)

Determinations of individual compounds

Obviously, it is not possible to cover here all the compounds which have been fluorimetrically determined and we have tried to present, in a fairly systematic fashion, some selected reactions in order to show that fluorimetry of individual compounds, as well as functional fluorimetry, is no longer a mere collection of purely empirical recipes. A definite compound has often been determined in various media (*e.g.*, biological assays), giving rise to sundry procedures based on the same reaction; quoting all the references would be but a compilation. As far as possible, we report the reference of the paper which, to the best of our knowledge, was the first dealing with this analytical reaction, or we refer to a paper reviewing it. We also mention some reactions which, until now, have only been used qualitatively, when we consider that they might readily be adapted to quantitative analysis.

It is well known that the main fluorescent species are either aromatic or heterocyclic compounds. Since it is usually easier to create a heterocyclic ring than an aromatic one, many determinations are based on the formation of a *O*- or *N*-heterocycle. Of course, some reactions are exceptions to this rule. For example, cerium(III) ions in dilute sulphuric acid medium exhibit a characteristic fluorescence, exc: 260 nm, em: 350 nm. Osmium(VIII) catalyses the redox reaction between cerium(IV) and oxalate, thus permitting a fluorimetric determination of oxalate ion by measurement of the cerium(III) produced.[92] Oxalate also quenches the fluorescence of a 1:1 zirconium–flavonol chelate in dilute sulphuric acid solution, the emission decreasing with increasing concentration of the ion.[93] In a similar manner, citrate quenches the fluorescence of the tungstate–flavonol complex.[94]

Some non-fluorescent acids and bases have been determined by ion-pair extraction with a fluorescent species as counter-ion. For example, dimethylprotriptyline (VIII) allowed the estimation of nonylbenzenesulphonate and tetradecansulphonate.[95]

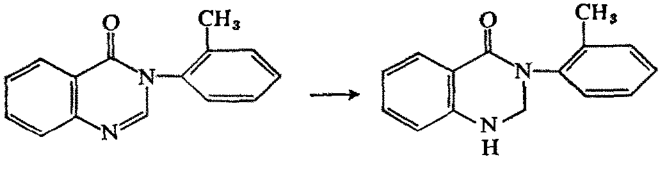


(VIII)

Protriptyline, nortriptyline, amitriptyline, imipramine and terodoline were determined with anthracene-2-sulphonate.[96]

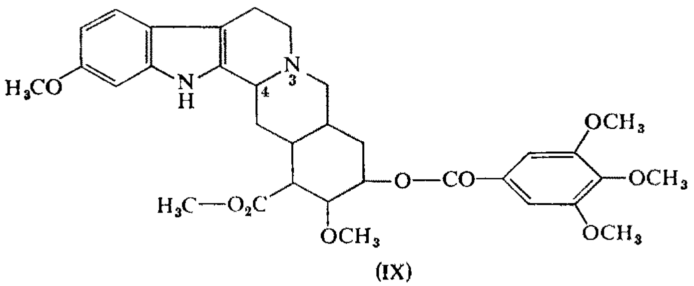
Obviously, some of the reactions described in the preceding section can be applied to the determination of a definite compound. For instance, J-acid or a mixture of ammonium acetate and ethyl acetoacetate or 2,4-pentanedione allow a selective determination of formaldehyde. The glyoxylic acid–resorcinol reaction[14] permits determination of oxalic acid, which can be reduced to glyoxylic acid by aluminium amalgam, a copper–zinc mixture,[97] or zinc and hydrochloric acid.[98] Glyoxylic acid is also obtained by saponifying dichloroacetic acid in the presence of hydrazine, which avoids formation of oxalic and glycolic acids. This reaction has been applied to the identification of the dichloroacetic group in chloramphenicol.[99]

A slight modification of the structure of a heterocyclic compound, such as a change in the degree of saturation can result in development or extinction of fluorescence. For example, methaqualone was determined as a tetrahydroquinazolinone derivative after reduction by lithium borohydride.[100]



Reserpine (IX) has a native fluorescence which permits direct measurements, but the emission maximum is at 375 nm. A more intense and yellow-green fluorescence (em: 510 nm) is obtained by a suitable 3-4 dehydrogenation, with hydrogen peroxide[101] or nitrous acid.[102,103]

Various heterocyclic compounds bearing a hydroxyl group fluoresce only in the free state. Esters must therefore be hydrolysed before fluorimetric determination. For instance, *O*,*O*-diethyl-*O*-(3-chloro-4-methyl-2-oxo-2*H*-1-benzopyran-7-yl)phosphorothioate (Coumaphos) affords fluorescent 3-chloro-4-methyl-7-hydroxycoumarin.[104] *O*,*O*-Diethyl-*O*-2-pyrazinyl phosphorothioate yields the sodium salt of 2-pyrazinol.[105] Tocopherol esters are also determined as free tocopherol. In order



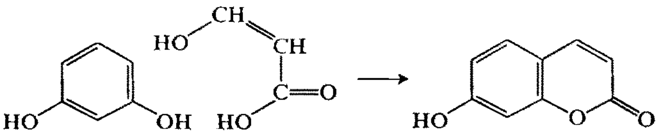
(IX)

to avoid oxidation, the esters are reduced to the free hydroxyl compound by lithium aluminium hydride.[106]

Diethyl phosphate ester and *O,O*-diethyl phosphorothioate *O*-ester with *N*-hydroxynaphthalimide (Maretin and Bayer 22408) are determined after alkaline hydrolysis followed by an oxidation step.[107,108]

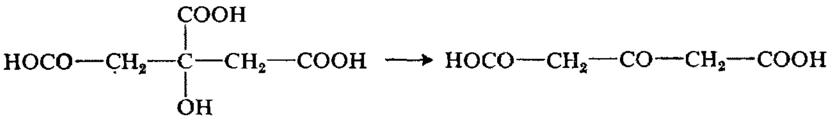
Formation of O-*heterocycles.* The von Pechmann reaction, used in functional fluorimetry for the estimation of phenols, has been applied to the determination of polycarboxylic acids which are unsaturated or bear hydroxyl groups. Malic acid, reacting with resorcinol in concentrated sulphuric acid, yields umbelliferone. In the first step, the acid is converted into formylacetic acid.

$$\mathrm{HOCO{-}CH_2{-}CHOH{-}COOH \rightarrow HOCO{-}CH_2{-}CHO}$$

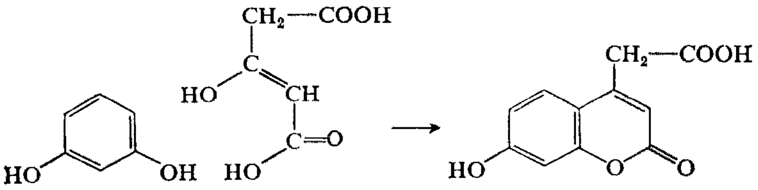


It has been claimed that umbelliferone-4-carboxylic acid is also formed.

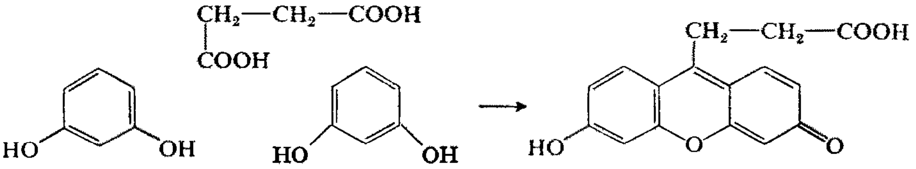
Likewise, citric acid gives a fluorescent species. The first step is probably to convert it into acetonedicarboxylic acid.



$$\mathrm{HOCO{-}CH_2{-}\underset{\displaystyle OH}{\overset{\displaystyle COOH}{C}}{-}CH_2{-}COOH \longrightarrow HOCO{-}CH_2{-}CO{-}CH_2{-}COOH}$$

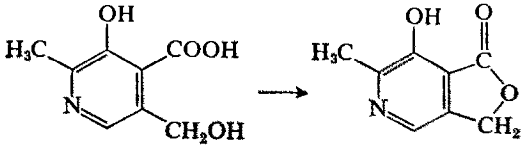


Fluorescences are also afforded by fumaric, α-oxoglutaric, oxalacetic acids, and polycarboxylic acids with no other functional groups. These react to produce compounds similar to fluorescein.



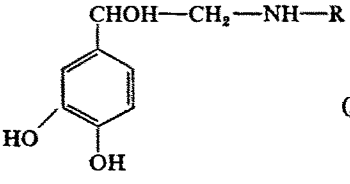
A convenient selection of pH and excitation and emission wavelengths allowed determination of malic and succinic acids in mixtures.[109] For a more selective determination of malic acid, orcinol[110,111] and 2-naphthol[112] have been proposed. With the last phenol, citric and succinic acids do not interfere at concentration ratios lower than 1:1. The fluorescent species is probably 5,6-benzocoumarin. With malic acid as the reagent, the same authors determined 2-naphthol.

Pyridoxic acid can be dehydrated in acidic medium to give a strongly fluorescent pyridoxic lactone.[113]



The lactone fluoresces 25 times as intensely as the acid. This is probably due to an increase in the quantum efficiency of fluorescence. Pyridoxic acid is obtained from pyridoxine oxidized with potassium permanganate, from pyridoxamine converted into pyridoxine with nitrous acid and then oxidized, and from pyridoxal oxidized with ammonical silver nitrate.[114] These three compounds can therefore be determined fluorimetrically.

Formation of N-*heterocycles.* One of the most studied determinations is probably that of catecholamines, mainly epinephrine (X) and norepinephrine (XI).

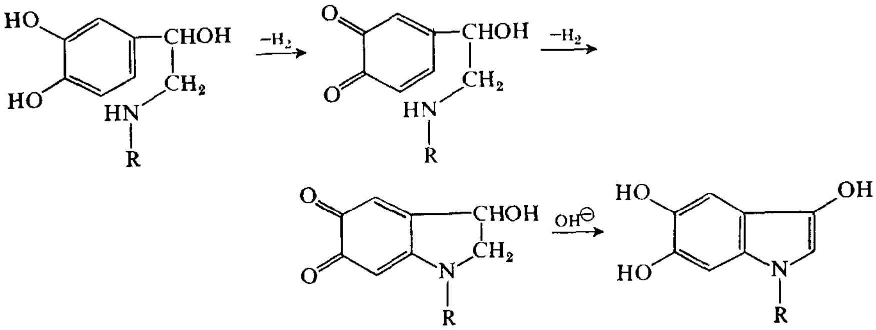


(X) $R = CH_3$
(XI) $R = H$

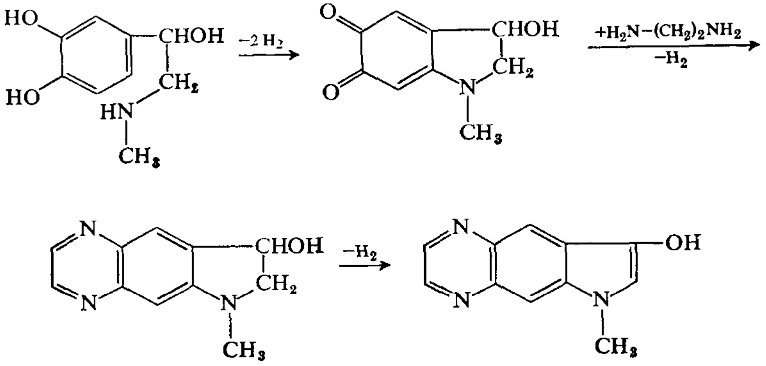
Epinephrine upon oxidation gives an *o*-quinone derivative, adrenochrome, which in alkaline medium is subjected to a rearrangement yielding adrenolutine, a strongly fluorescent trihydroxyindole derivative.[115]

The same reaction can of course be applied to norepinephrine. Differential determinations are possible, since both amines are oxidized at pH 6·5, whereas only epinephrine reacts at pH 3·5.[116]

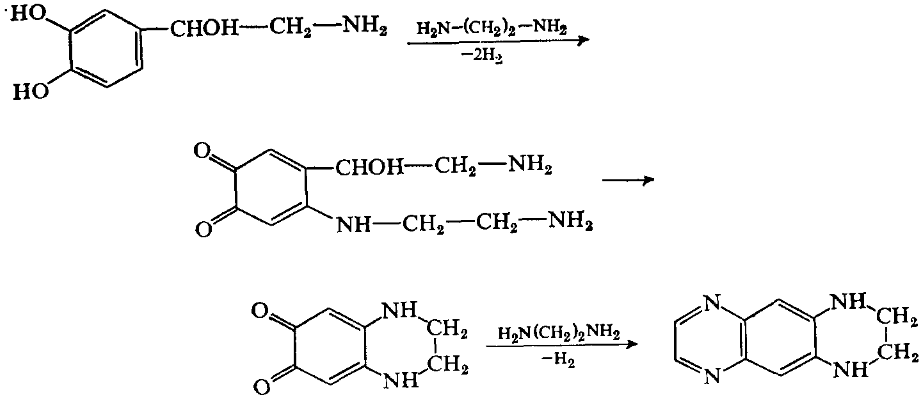
In the presence of ethylenediamine, other fluorescent species are obtained, and the mechanisms of the reactions are different for epinephrine and norepinephrine.[117]



Epinephrine

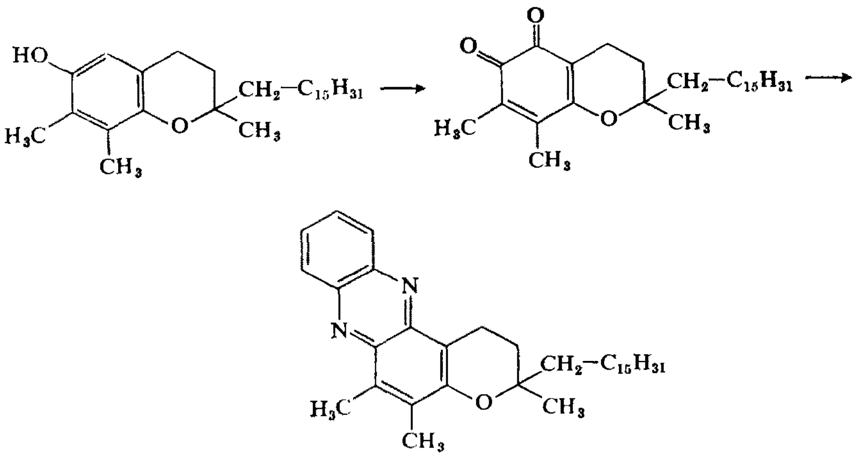


Norepinephrine

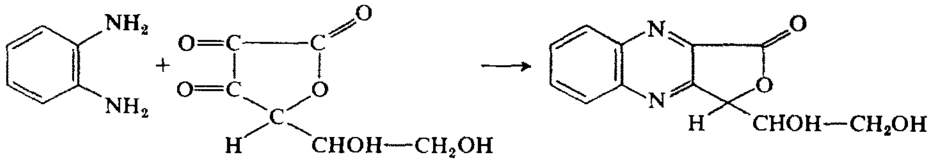


Another fluorescent product is also formed, the structure of which is not yet certain. By suitable selection of emission wavelengths, both compounds can be determined in mixtures. The method has recently been automated.[118] On the same basis, with adrenochrome as reagent, ethylenediamine has been determined in milk.[119]

Another diamine, *o*-phenylenediamine, reacts with some *o*-quinones and α-diketo derivatives, to yield strongly fluorescent species. Tocopherol, oxidized with nitric acid, gives a quinone which is then condensed with *o*-phenylenediamine to give a phenazine derivative.[120]

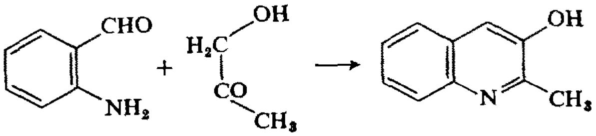


Ascorbic acid is oxidized to dehydroascorbic acid which, upon reacting with the same diamine, produces a fluorescent quinoxaline, thus permitting the determination of the vitamin.[121]



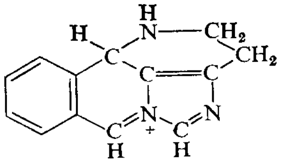
Alloxan was also determined by a similar reaction.[112]

Two other *o*-disubstituted benzenes have been used as reagents for various purposes. *o*-Aminobenzaldehyde reacts with acetol to form fluorescent 3-hydroxyquinaldine.[123]

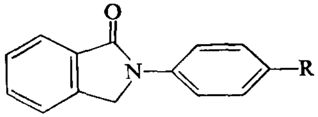


Thymine and 5-methylcytosine, when suitably oxidized, afford this ketol[124] and can therefore be determined as well as nucleosides and nucleotides of these pyrimidines, and deoxyribonucleic acid.[125] *o*-Phthalaldehyde gives a fluorescent adduct upon condensation with histamine. The formula (XII) has been tentatively proposed.[126]

Under suitable conditions, histamine can readily be determined in the presence of histidine, which normally interferes[127] and histidine has also been determined.[128]



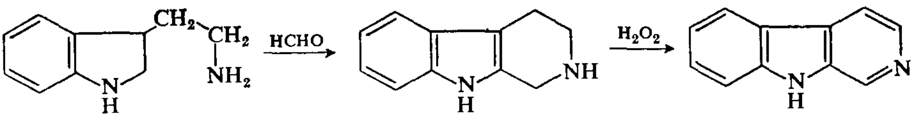
(XII)



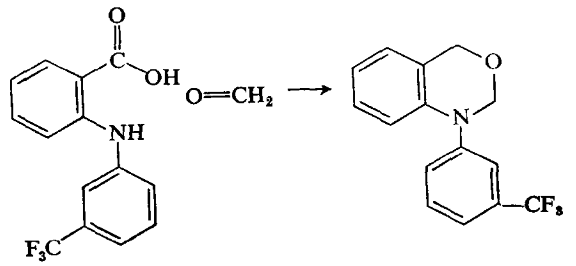
(XIII)

The same reagent has been applied to the determination of some sulphonamides, which give condensates of general formula (XIII),[129] of α,ε-diaminopimelic acid,[130] and of reduced gluthathione.[131] In pH 8 medium, this tripeptide yields a fluorescent product whereas little or no fluorescence is observed from oxidized glutathione and thiol-containing amino-acids.

One of the simplest organic compounds, formaldehyde, has often been applied to various determinations. Examples were described above in the section on functional fluorimetry. Tryptamine offers a native fluorescence, but in various extracts, other species may interfere. These interferences may be overcome by reacting tryptamine with formaldehyde, then oxidizing the tetrahydronorharman formed to fluorescent norharman.[132]



Flufenamic acid also reacts with formaldehyde, giving a fluorescent heterocyclic derivative.[133]

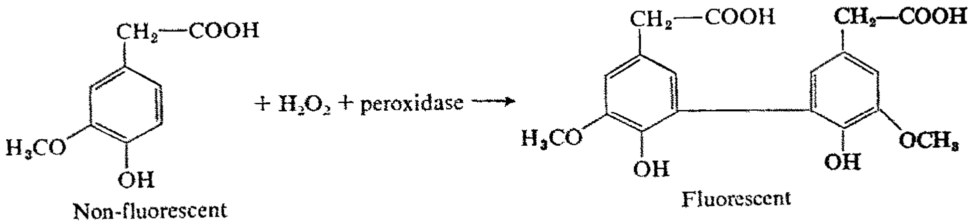


Many determinations, mainly in the field of steroid compounds, are conducted in strongly acidic media, such as concentrated sulphuric, phosphoric or perchloric acids. These "halofluoric" reactions are often due to various preferential mesomeric forms or to dehydrations which have mechanisms that are as yet not well understood. For these reasons, they are somewhat beyond the scope of this review. They have been already widely referred to in books and monographs.[5,9,116,134]

Enzymatic reactions

Studies on fluorimetric assay of enzymes, and enzyme kinetics and mechanisms are also beyond the scope of this review, since they are more closely related to biochemistry and biology. But recently, some enzymatic reactions have been applied to various fluorimetric determinations of organic compounds, thus paving the way to new methods which stand on the border of functional fluorimetry and fluorimetry of definite compounds.

Non-fluorescent homovanillic acid, reacting with hydrogen peroxide in the presence of horseradish peroxidase, gives a fluorophore by the following reaction:[135]

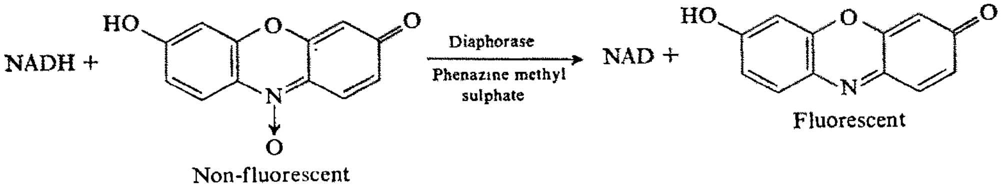


Compounds which upon action of suitable oxidases afford hydrogen peroxide, may therefore be determined. This is the case with xanthine and hypoxanthine when converted into uric acid by xanthine oxidase.[136]

The much cheaper *p*-hydroxyphenylacetic acid may be used instead of homovanillic acid. It allows the determination of *N*-acetyl-D-galactosamine, 2-deoxy-D-galactose, 2-deoxy-D-glucose, D-galactosamine, D-galactose, D-glucose, α-D-melibiose, methyl-β-D-galactopyranoside, D-raffinose, stachyose, sucrose. All these sugars, after invertase hydrolysis, are oxidized by glucose- or galactose-oxidase. The first is highly specific, whereas with galactose oxidase the C_1 position need not be free, for galactosides are readily attacked. The correct configuration at position 4 is essential, but that at position 2 is not so critical, for D-talose also reacts.[137]

Nicotinamide adenine dinucleotide (NAD), reacting with an acid under the action of a suitable dehydrogenase, is reduced to NADH which, under the catalytic action of diaphorase or phenazine methyl sulphate, reduces non-fluorescent resazurin to fluorescent resorufin. Six dehydrogenase systems were used for the determinations of 21 organic acids.[138]

$$\text{Acid} + \text{NAD} \xrightarrow{\text{Dehydrogenase}} \text{Keto acid} + \text{NADH}$$

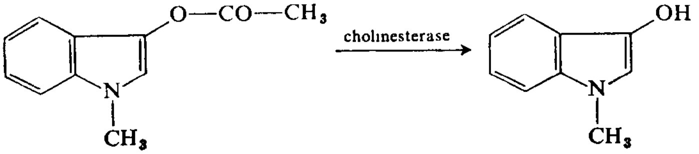


Monoamine and diamine oxidases allow the determination of benzylamine, cadaverine, furfurylamine, histamine, putrescine and tyramine,[139] hydrogen peroxide being formed.

$$R—CH_2—NH_2 + O_2 + H_2O \xrightarrow[\text{oxidase}]{\text{Amine}} R—CHO + NH_3 + H_2O_2$$

Methanol, ethanol, n-propanol and allyl alcohol have been determined with alcoholoxidase, which converts them into the corresponding aldehyde and hydrogen peroxide.[140]

Various pesticides have also been determined. Cholinesterase from rat liver and human serum is strongly inhibited by organophosphorus compounds, but the chlorinated pesticides have no effect. The enzyme from electric eel is sensitive to chlorinated pesticides only. Cholinesterases from both the bean-leaf beetle and white-fringe beetle are very strongly inhibited by paraoxon (diethyl-*p*-nitrophenylphosphate) and DDVP (phosphoric acid 2,2-dichlorovinyl dimethyl ester), but parathion and methyl parathion are very weak inhibitors. There is no interference either from the chlorinated or carbamate pesticides. The substrate *N*-methylindoxyl acetate is cleaved by all five cholinesterases to highly fluorescent *N*-methylindoxyl.



The various pesticides, when introduced into the reaction mixture, inhibit the hydrolysis of the substrate catalysed by cholinesterase, causing a decrease in the initial slope of the fluorescence-time curve. The decrease is a direct measure of the concentration of the inhibitor present.[141]

PHOSPHORIMETRY

Phosphorescence is the photon emission from a molecule which returns to its normal ground state from an excited triplet state, reached by a radiationless transfer from an excited singlet state. Whereas fluorescence decays almost immediately, usually within about 10^{-8} sec, the lifetime of phosphorescence is much longer, from 10^{-4} up to 20 sec. The first phosphoroscope was described a century ago,[142] but the qualitative identification of organic compounds by phosphorescence spectra was suggested only in 1944[143] and the first quantitave determinations were published in 1957.[144]

Since fewer compounds phosphoresce than fluoresce, phosphorimetry is still more selective than fluorimetry. In a solid solution, the phosphorescence decay process is of the first order. The mean decay time at constant temperature in a given solvent being characteristic of the compound studied (and independent of concentration), it can be used to identify phosphorescent compounds, thus introducing a complementary datum, besides the excitation and emission spectra. A pure substance alone will show a straight-line plot of the logarithm of intensity against time. With mixtures, a curved plot is obtained, since several decay processes with different rates are superimposed.[145]

Because of the long lifetime of phosphorescence, molecules can easily lose their energy by radiationless processes, mainly by collisional deactivation. Although some attempts were made at room temperature with rigid transparent organic glasses (polymeric matrices),[146] phosphorescence measurements are almost always performed at 77 K (liquid nitrogen). Until very recently, determinations were only possible in solvents and mixtures of solvents giving clear glasses at this temperature. Various mixtures have been proposed,[147] but they often tend to crack or form snows when they contain a small quantity of water. Absolute ethanol has proved very suitable, since its water content is not highly critical.[148] In 1970, the use of a rotating sample cell was proposed.[149] Combined with a more stable power supply and a better solvent clean-up procedure, it led to lowering of detection limits by more than a factor of 100, and to increased precision and accuracy. Moreover, these results have been obtained not only in clear rigid solvents, but also in cracked glasses and snowed matrices.

Up to now, and to the best of our knowledge, phosphorimetry has only been applied to the estimation of compounds offering a native phosphorescence. The potentialities of the method in the field of quantitative determinations were first exemplified with benzaldehyde, benzophenone and 4-nitrobiphenyl dissolved in EPA (ethyl ether–isopentane–ethanol 5:5:2).[144] In a mixture of these three compounds, 4-nitrobiphenyl could be resolved on the basis of its slower decay rate. Mixtures of acetophenone and benzophenone were also resolved, the mean lifetimes of these compounds being 0·008 and 0·006 sec respectively. Diphenylamine and triphenylamine were determined by selective excitation.

As a consequence of its selectivity and sensitivity, phosphorimetry has been mainly applied in the areas of biology and medicine. Aspirin was the first compound to be determined in blood and plasma, without interference, at concentrations of 1–100 mg per 100 ml of serum.[150] Salicylic acid, the only metabolic product of aspirin which phosphoresces, gave nearly 1/500 the sensitivity of aspirin. The use of ethanol allowed easy determinations of 22 organic compounds of pharmacological importance, with a limit of detectability of 10 ng/ml in ethanol for most drugs.[148] Procaine, cocaine, phenobarbital and chlorpromazine have been determined in blood serum, and cocaine and atropine in urine.[151] The proposed method is rapid and sensitive. For instance, it allows 83% recovery of 0·30 μg of procaine in 10 ml of blood, or 110% recovery of 30 ng of cocaine in 1 ml of blood. Sulphonamides have been determined.[152] and for sulphamerazine, sulphapyridine, sulphamethazine and sulphacetamide, the limit of detectability was 0·1 ng/ml of solvent.

Tobacco samples have been analysed for nicotine, nornicotine and anabasine.[153] The method involves a separation by thin-layer chromatography, and the time for a complete analysis of the three alkaloids in a commercial tobacco sample was less than 90 min, which is considerably less than by other methods previously used. In the field of pesticides, 32 compounds have been studied,[154] and biphenyl has been determined in oranges, with a limit of 1 ng/ml of ethanol.[155]

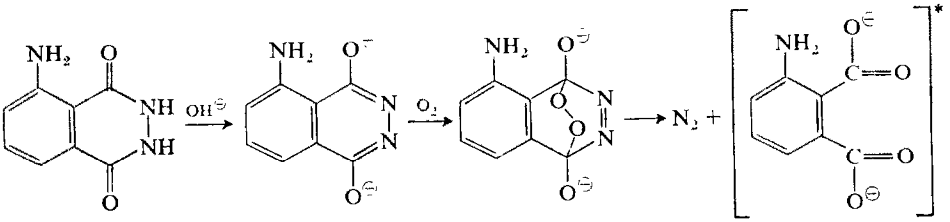
Mixtures of tryptophan and tyrosine in the presence of phenylalanine in various hydrolysed proteins have been analysed simultaneously.[156] The method is based on the fact that when two molecules differ by approximately a factor of 10 in their decay times, and when the concentrations of the species are about equal, a plot of the logarithm of the phosphorescence intensity *vs.* time is a combination of two straight lines.

This section is far from being exhaustive. Our purpose was only to illustrate the possibilities and potentialities of phosphorimetry. There is no doubt that commercially available phosphoroscope attachments, and the recent possibility of working with cracked glasses and snowed matrices will extend the usefulness of this method, both in the areas of biology and medicine, where sensitive, selective, accurate and rapid methods are needed, and in other areas for the study of trace impurities.

CHEMILUMINESCENCE

In fluorescence and phosphorescence, the activation of the molecule is obtained by the absorption of light. In chemiluminescence, the excitation is produced by a chemical reaction. Although this phenomenon has been widely studied,[157–159] only a few examples are within the scope of this review.

Luminol(5-amino-2,3-dihydro-1,4-phthalazinedione) emits light when oxidized in alkaline medium under suitable conditions. Various mechanisms have been proposed,[160–162] and it has been shown that, under aqueous conditions with hydrogen peroxide, the reaction products are complex.[163] Whatever may be the true mechanism, it is established that the luminescence is afforded by an excited singlet state of the aminophthalate ion. The following scheme seems possible:



When copper(II) is added to an alkaline solution of luminol in the presence of hydrogen peroxide, the mixture emits light, and this emission is inhibited by various compounds. The effect of small amounts of nitrophenols, aminophenols, trihydroxybenzenes, dinotrophenols, nitroanilines and phenylenediamines on the chemiluminescence of the system luminol-Cu-NH_3-H_2O_2 has also been studied.[164] All these compounds inhibit the luminescence and, for disubstituted derivatives, the order of the inhibiting action is *ortho* > *para* > *meta*. Small amounts of the compounds can be determined by means of a calibration graph. Polyhydric alcohols, unsaturated monohydric alcohols, mono- and disaccharides are also effective.[165] α-Amino-acids have been determined, the reaction being based on the reduction of the intensity of luminescence of luminol in the presence of cupric sulphate in dilute ammonia and hydrogen peroxide. The intensity of inhibition varies with the amino-acid tested.[166] Copper complexes of amino-acids have also been determined.[167]

Adenosine triphosphate reacts with luciferin in the presence of magnesium ion and luciferase, under the action of oxygen:

$$\text{Luciferin} + O_2 + \text{ATP} \xrightarrow[\text{Mg}^{2+}]{\text{Luciferase}} \text{Oxyluciferin} + \text{AMP} + h\nu.$$

Measurement of the light produced gives a direct determination of the ATP present.[168]

Ozone-induced chemiluminescence of organic compounds has also been studied, in the dry state as well as in acetone solution.[169] The peak intensity of the light emission is related quantitatively to the amount of compound.

Up to now, with the exception of the ATP determination, the proposed methods do not seem to be more sensitive than fluorimetric ones.

APPENDIX

Determination of primary and secondary alkylamines

Reagent. A 0·05% solution of 4-chloro-7-nitrobenzofurazan in ethanol.

Procedure. To 1 ml of an ethanol solution of the amine, add 0·75 ml of reagent. Heat at 60° for 30 min, in daylight, then let stand for 3 min at room temperature, dilute to 4 ml with ethanol and read at exc: 436 nm, em: 535 nm (yellow fluorescence). The fluorescence standard is an aqueous solution of sodium fluoresceinate

Results

	Determination limits, μg	Reading 50 Sample, μg	Standard, μg/ml
n-Propylamine	0·25–1·0	0·41	0·12
n-Butylamine	0·25–1·0	0·45	0·12
Benzylamine	0·25–1·0	0·41	0·083
Diethylamine	1–5	1·9	0·083
Di-n-propylamine	3–12	4·3	0·13
Di-n-butylamine	2–10	4·0	0·06

Determination of primary alkylamines

Buffer, pH 8·6. Dissolve 0·62 g of boric acid and 0·745 g of potassium chloride in 50 ml of water, add 12·0 ml of 0·2*M* sodium hydroxide and dilute with water to a final volume of 200 ml.

Reagent. A 0·25% solution of *o*-diacetylbenzene in ethanol.

Procedure. To 1 ml of an ethanol solution of the amine or amine hydrochloride, add 0·5 ml of buffer and 0·2 ml of reagent. Heat at 30° for 60 min, cool to room temperature and add 2 ml of ethanol. Read at exc: 366 nm, em: 430 nm (blue fluorescence). The fluorescence standard is a solution of quinine sulphate in 0·1*N* sulphuric acid.

Results

	Determination limits, μg	Reading 50 Sample, μg	Standard, μg/ml
Methylamine (hydrochloride)	0·2–1·0	0·43	0·256
Ethylamine	0·1–0·5	0·22	0·238
Ethylamine (hydrochloride)	0·2–1·0	0·44	0·227
n-Propylamine	0·1–0·5	0·21	0·164
n-Butylamine	0·2–1·0	0·44	0·222

Determination of primary arylamines

Reagents. (*a*) 0·50% aqueous solution of the sodium salt of 1,2-naphthoquinone-4-sulphonic acid. (*b*) Dissolve 0·050 g of potassium borohydride in 1 ml of 0·1*M* sodium hydroxide and dilute to 100 ml with water.

Procedure. To 1 ml of a neutral aqueous solution of the arylamine, add 0·2 ml of reagent *a*, mix, and transfer into a 10-ml separatory funnel which contains 2 ml of methylene chloride. Rinse the tube with 1 ml of water, adding the rinsings to the separatory funnel. Shake for about 5 sec, allow the layers to separate and drain all of the organic layer into a tube. With the tube protected from light, add 2 ml of ethanol, 0·1 ml of reagent *b*, mix, and let stand for 1 min at room temperature. Add 0·5 ml of 0·01*M* hydrochloric acid and mix. Read at exc: 366 nm, em: 470 nm (blue-green fluorescence). The fluorescence standard is a solution of 3,5-dicarbethoxy-1,4-dihydrolutidine in water containing 2% ethanol (see Ref. 14).

Results

	Determination limits, *μg*	Reading 50 Sample, *μg*	Standard, *μg/ml*
Aniline	0·2–1·0	0·48	1·89
o-Toluidine	0·3–1·5	0·72	1·92
m-Toluidine	0·2–1·0	0·48	1·64
p-Toluidine	0·2–1·0	0·48	1·67
p-Anisidine	0·3–1·5	0·73	1·85
o-Aminophenol	0·2–1·0	0·48	1·82

Arylamines bearing substituents which favour solubility in slightly alkaline water, such as *p*-aminobenzoic acid and sulphonamide, do not react.

Determination of monosubstituted guanidines

Reagent. A 0·05 % solution of phenanthrenequinone in ethanol.

Procedure. To 0·5 ml of an aqueous solution of the guanidine, add 0·1 ml of 40 % sodium hydroxide solution and 0·5 ml of reagent. Mix and let stand for 30 min at room temperature. Add 0·25 ml of concentrated hydrochloric acid and 2·5 ml of water. Mix and read at exc: 360 nm, em: 400 nm. Any slight turbidity in the solution does not interfere with measurements (violet-blue fluorescence). The fluorescence standard is a solution of quinine sulphate in 0·1*N* sulphuric acid.

Results

	Determination limits, *μg*	Reading 50 Sample, *μg*	Standard, *μg/ml*
Arginine	1·5–7·5	3·0	1·66
p-Chlorophenylguanidine	37·5–150	63·7	2·28
Dihydrostreptomycin (sulphate)	16–80	32	1·82
Guanethidine (sulphate)	2–10	4	2·27
Guanidine	1·5–6·0	2·5	2·7
Guanidoacetic acid	0·8–4·0	1·6	1·9
Streptomycin (sulphate)	15–60	22·5	2·1
3,4,5-Trimethoxybenzylguanidine	2–10	4·2	2·2

Determination of ketoses

Reagent. A 0·1 % aqueous solution of zirconyl chloride.

Procedure. To 1 ml of an aqueous solution of the ketose, add 0·7 ml of 0·01*M* hydrochloric acid and 0·5 ml of reagent, mix and add 2 ml of water. Heat at 70° for 60 min, cool in ice for 2 min and read at exc: 345 nm, em: 400 nm (blue fluorescence). The fluorescence standard is a solution of quinine sulphate in 0·1*N* sulphuric acid.

Results

	Determination limits, *μg*	Reading 50 Sample, *μg*	Standard *μg/ml*
Fructose (1 H_2O)	6–24	9·3	0·115
Sorbose	6–30	12·9	0·071

Zusammenfassung—In dieser Übersicht werden die wichtigen Aspekte der Lumineszenzverfahren behandelt, die zur Bestimmung organischer Verbindungen in Lösung dienen können. Ein Bezeichnungsschema für Berichte über fluorimetrische Bestimmungen wird vorgeschlagen. Es wird eine kurze Übersicht über die wesentlichen Faktoren gegeben, die die Fluoreszenz von Lösungen beeinflussen; ausgewählte Beispiele illustrieren die Bestimmung von Verbindungen, die von Hause aus fluoreszieren. Besonderer Wert wird auf die Fluorimetrie funktioneller Gruppen gelegt und auf die Bestimmung nicht fluoreszierender Verbindungen mit Hilfe chemischer Reaktionen, die zu fluoreszierenden Spezies führen. Einige enzymatische Reaktionen werden beschrieben, soweit sie die Bestimmung definierter chemischer Verbindungen erlauben. Beispiele für Phosphorimetrie und Chemilumineszenz werden angeführt. Ein Anhang zeigt einige neu von den Autoren entwickelte fluorimetrische Bestimmungsmethoden für funktionelle Gruppen.

Résumé—Cette revue présente les principaux caractères des méthodes de luminescence se rapportant au dosage de composés organiques en solution. On propose une notation pour rapporter les dosages fluorimétriques. On passe brièvement en revue les facteurs dominants qui affectent la fluorescence des solutions, et l'on illustre par des exemples choisis les dosages de composés à fluorescence native. On porte une attention particulière à la fluorimétrie fonctionnelle et au dosage de composés non fluorescents au moyen de réactions chimiques donnant naissance à des espèces fluorescentes. On décrit quelques réactions enzymatiques, dans la mesure où elles permettent le dosage de produits chimiques définis. La phosphorimétrie et la chimiluminescence sont illustrées par des exemples. Un appendice présente quelques nouveaux dosages de fluorimétrie organique fonctionnelle, développés par les auteurs.

REFERENCES

1. C. E. White, *Anal. Chem.*, 1970, **42**, 57R.
2. D. M. Hercules, *Fluorescence and Phosphorescence Analysis*, Interscience, New York, 1966.
3. R. Bourdon, *Mises au Point de Chimie Analytique, 15e série*, p. 1. Masson, Paris, 1967.
4. C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam, 1968.
5. M. Pesez, *Mises au Point de Chimie Analytique, 17e série*, p. 172. Masson, Paris, 1968.
6. E. Sawicki, *Talanta*, 1969, **16**, 1231.
7. M. Pesez, *Farmaco (Pavia) Ed. Prat.*, 1970, **25**, 205.
8. *Idem.*, *Cronache di Chimica (Milano)*, 1970, **28**, 12.
9. C. E. White and R. J. Argauer, *Fluorescence Analysis*, Dekker, New York, 1970.
10. T. Momose and Y. Ohkura, *Talanta*, 1959, **3**, 151.
11. R. A. Chalmers and G. A. Wadds, *Analyst*, 1970, **95**, 234.
12. E. Sawicki and R. A. Carnes, *Mikrochim. Acta*, 1968, 148.
13. *Idem*, *ibid.*, 1968, 602.
14. M. Pesez and J. Bartos, *Talanta*, 1967, **14**, 1097.
15. B. L. van Duuren, *Chem. Rev.*, 1963, **63**, 325.
16. *Idem*, *J. Org. Chem.*, 1961, **26**, 2954.
17. R. F. Chen, *Arch. Biochem. Biophys.*, 1967, **120**, 609.
18. A. S. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1960, **24**, 591.
19. G. Oster and Y. Nishijima, *J. Am. Chem. Soc.*, 1956, **78**, 1581.
20. R. Livingston, W. F. Watson and J. McArdle, *ibid.*, 1949, **71**, 1542.
21. H. Kokubun, *Z. Physik. Chem. Frankfurt*, 1957, **13**, 386.
22. J. J. Surash and D. M. Hercules, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 1961.* Cf. ref. (15), p. 332.
23. See ref. (2), p. 37.
24. E. Sawicki, T. W. Stanley and W. C. Elbert, *Talanta*, 1967, **14**, 431.
25. S. G. Schulman and J. D. Wineforder, *ibid.*, 1970, **17**, 607.
26. C. A. Parker and W. J. Barnes, *Analyst*, 1957, **82**, 606.
27. B. Stevens and J. T. Dubois, *Trans. Faraday Soc.*, 1963, **59**, 2813. See also ref. (2), p. 106.
28. J. de Ment, *Fluorochemistry*, Chemical Publishing Co., New York, 1945.
29. D. J. W. Grant and J. C. Patel, *Anal. Biochem.*, 1969, **28**, 139.

30. G. A. Thommes and E. Leininger, *Anal. Chem.*, 1958, **30**, 1361.
31. S. Udenfriend, D. F. Bogdanski and H. Weissbach, *Science*, 1955, **122**, 972.
32. E. Sawicki, T. W. Stanley and J. Pfaff, *Anal. Chim. Acta*, 1963, **28**, 156.
33. C. I. Miles and G. H. Schenk, *Anal. Chem.*, 1970, **42**, 656.
34. D. M. Hercules and L. B. Rogers, *ibid.*, 1958, **30**, 96.
35. E. Sawicki, T. W. Stanley and H. Johnson, *Mikrochim. Acta*, 1965, 178.
36. E. Sawicki, H. Johnson and K. Kosinski, *Microchem. J*, 1966, **10**, 72.
37. G. H. Schenk and D. R. Wirz, *Anal. Chem.*, 1970, **42**, 1754.
38. C. A. Parker, *Analyst*, 1959, **84**, 446. See also ref. (4), p. 64 and 411.
39. M. Pesez and J. Bartos, *Talanta*, 1969, **16**, 331.
40. *Idem*, unpublished results.
41. H. Meerwein, K. Wunderlich and K. F. Zenner, *Angew. Chem.*, 1962, **74**, 807.
42. M. Pesez and J. Bartos, *Bull. Soc. Chim. France*, 1963, 2333.
43. E. Sawicki and R. A. Carnes, *Anal. Chim. Acta*, 1968, **41**, 178.
44. J. T. Stewart and D. M. Lotti, *ibid.*, 1970, **52**, 390.
45. See ref. (9), pp. 180–3.
46. N. Seiler and M. Wiechmann, *Z. Anal. Chem.*, 1966, **220**, 109.
47. P. B. Ghosh and M. W. Whitehouse, *Biochem. J.*, 1968, **108**, 155.
48. M. Pesez and J. Bartos, *Ann. Pharm. Franç.*, 1969, **27**, 161.
49. J. Bartos, *ibid.*, 1969, **27**, 691.
50. R. B. Conn and R. B. Davis, *Nature*, 1959, **183**, 1053.
51. K. Beyermann and H. Wisser, *Z. Anal. Chem.*, 1969, **245**, 311.
52. F. de Fabrizio, *J. Pharm. Sci.*, 1969, **58**, 136.
53. S. Yamada and H. A. Itano, *Biochem. Biophys. Acta*, 1966, **130**, 538.
54. J. Bartos, *Bull. Soc. Chim. France*, 1965, 3694.
55. *Idem*, *Ann. Pharm. Franç.*, 1970, **28**, 321.
56. H. J. Bielig and E. Bayer, *Ann.*, 1953, **584**, 96.
57. F. Feigl, *Spot Tests in Organic Analysis, 7th ed.*, p. 174. Elsevier, Amsterdam, 1966.
58. M. Stiller, *Anal. Chim. Acta*, 1961, **25**, 85.
59. J. Balog and J. Császár, *Magyar Kem. Folyoirat*, 1961, **67**, 62.
60. M. Pesez and J. Bartos, *Bull. Soc. Chim. France*, 1961, 1930.
61. J. Bartos, *Ann. Pharm. Franç.*, 1969, **27**, 323.
62. O. Zima, K. Ritsert and T. Moll, *Hoppe-Seyler's Z. Physiol. Chem.*, 1941, **267**, 210.
63. K. Kono, *J. Vitaminol. (Japan)*, 1966, **12**, 137.
64. G. M. Badger, H. P. Crocker, B. C. Ennis, J. A. Gayler, W. E. Matthews, W. G. C. Raper, E. L. Samuel and T. M. Spotswood, *Australian J. Chem.*, 1963, **16**, 814.
65. T. P. Forrest, G. A. Dauphinee and W. F. Miles, *Can. J. Chem.*, 1969, **47**, 2121.
66. L. Velluz, M. Pesez and M. Herbain, *Bull. Soc. Chim. France*, 1948, **15**, 681.
67. L. Velluz, G. Amiard and J. Bartos, *J. Biol. Chem.*, 1949, **180**, 1137.
68. R. A. Salvador and R. W. Albers, *J. Biol. Chem.*, 1959, **234**, 922.
69. M. Pesez, *Bull. Soc. Chim. Biol.*, 1950, **32**, 701.
70. J. M. Kissane and E. Robins, *J. Biol. Chem.*, 1958, **233**, 184.
71. M. Blecher, *Anal. Biochem.*, 1961, **2**, 30.
72. F. B. Cramer and G. A. Neville, *J. Franklin Inst.*, 1953, **256**, 379.
73. H. H. Hess and E. Rolde, *J. Biol. Chem.*, 1964, **239**, 3215.
74. R. A. Braun and W. A. Mosher, *J. Am. Chem. Soc.*, 1958, **80**, 2749, 3048.
75. R. Brandt and N. D. Cheronis, *Microchem. J.*, 1961, **5**, 110.
76. D. J. Pietrzyk and E. P. Chan, *Anal. Chem.*, 1970, **42**, 37.
77. J. E. Spikner and J. C. Towne, *ibid.*, 1962, **34**, 1468.
78. S. Mizutani, Y. Wakuri, N. Yoshida, T. Nakajima and Z. Tamura, *Chem. Pharm. Bull. (Japan)*, 1969, **17**, 2340.
79. J. Bartos, *Ann Pharm. Franç.*, 1971, **29**, 221.
80. *Idem*, *ibid.*, 1971, **29**, 71.
81. R. P. Maickel and F. P. Miller, *Anal. Chem.*, 1966, **38**, 1937.
82. T. J. Mellinger and C. E. Keeler, *ibid.*, 1963, **35**, 554.
83. J. B. Ragland, V. J. Kinross-Wright and R. S. Ragland, *Anal. Biochem.*, 1965, **12**, 60.
84. E. A. Martin, *Can. J. Chem.*, 1967, **45**, 75.
85. J. C. Towne and J. E. Spikner, *Anal. Chem.*, 1963, **35**, 211.
86. C. J. Rogers, C. W. Chambers and N. A. Clarke, *ibid.*, 1966, **38**, 1851.
87. T. Momose and Y. Ohkura, *Chem. Pharm. Bull.*, 1959, **7**, 31.
88. *Idem*, *ibid.*, 1958, **6**, 412.
89. H. Trapmann and V. S. Sethi, *Z. Anal. Chem.*, 1969, **248**, 314.
90. M. Maeda, T. Kinoshita and A. Tsuji, *Anal. Biochem.*, 1970, **38**, 121.

91. K. Schlossmann, *Arzneimittelforsch.*, 1967, **17**, 234.
92. G. F. Kirkbright, T. S. West and C. Woodward, *Anal. Chim. Acta*, 1966, **36**, 298.
93. D. A. Britton and J. C. Guyon, *ibid.*, 1969, **44**, 397.
94. J. C. Guyon and J. Y. Marks, *Mikrochim. Acta*, 1969, 731.
95. K. O. Borg, *Acta Pharm. Suecica*, 1969, **6**, 425.
96. K. O. Borg and D. Westerlund, *Z. Anal. Chem.*, 1970, **252**, 275.
97. M. Pesez, *Bull. Soc. Chim. France*, 1936, **3**, 676, 2072.
98. P. M. Zarembski and A. Hodgkinson, *Biochem. J.*, 1965, **96**, 218, 717.
99. M. Pesez, *Ann. Pharm. Franç.*, 1951, **9**, 187.
100. S. S. Brown and G. A. Smart, *J. Pharm. Pharmacol.*, 1969, **21**, 466.
101. E. B. Dechene, *J. Am. Pharm. Assoc. Sci. Ed.*, 1957, **44**, 657.
102. R. P. Haycock, P. B. Sheth, R. J. Connolly and W. J. Mader, *J. Agr. Food Chem.*, 1966, **14**, 437.
103. B. N. Kabadi, A. T. Warren and C. H. Newman, *J. Pharm. Sci.*, 1969, **58**, 1127.
104. C. A. Anderson, J. M. Adams and D. MacDougall, *J. Agr. Food Chem.*, 1959, **7**, 256.
105. U. Kiigemagi and L. C. Terriere, *ibid.*, 1963, **11**, 293.
106. D. E. Duggan, *Arch. Biochem. Biophys.*, 1959, **84**, 116.
107. R. J. Anderson, C. A. Anderson and M. L. Yagelowich, *J. Agr. Food Chem.*, 1966, **14**, 43.
108. P. A. Giang, *ibid.*, 1961, **9**, 42.
109. C. G. Barr, *Plant Physiol.*, 1948, **23**, 443.
110. J. P. Hummel, *J. Biol. Chem.*, 1949, **180**, 1225.
111. M. Strassman and L. Ceci, *Methods in Enzymol.*, 1969, **13**, 526.
112. E. Leininger and E. Katz, *Anal. Chem.*, 1949, **21**, 1375.
113. J. W. Huff and W. A. Perlzweig, *J. Biol. Chem.*, 1944, **155**, 345.
114. A. Fujita, K. Matsuura and K. Fujino, *J. Vitaminol. (Osaka)*, 1955, **1**, 267; A. Fujita, D. Fujita and K. Fujino, *ibid.*, 1955, **1**, 275, 279.
115. A. Lund, *Acta Pharmacol. Toxicol.*, 1949, **5**, 75, 1218.
116. S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, p. 143. Academic Press, New York, 1962.
117. H. Weil-Malherbe, *Biochim. Biophys. Acta*, 1960, **40**, 351.
118. J. K. Viktora, A. Baukal and F. W. Wolff, *Anal. Biochem.*, 1968, **23**, 513.
119. N. R. Pasarela and A. C. Waldron, *J. Agr. Food Chem.*, 1967, **15**, 221.
120. M. Kofler, *Helv. Chim. Acta*, 1942, **25**, 1469; 1943, **26**, 2166; 1945, **28**, 26; 1947, **30**, 1053.
121. M. J. Deutsch and C. E. Weeks, *J. Assoc. Offic. Agr. Chem.*, 1965, **48**, 1248.
122. R. M. Archibald, *J. Biol. Chem.*, 1945, **158**, 347.
123. O. Baudisch, *Biochem. Z.*, 1918, **89**, 279.
124. H. J. Deuel and O. Baudisch, *J. Am. Chem. Soc.*, 1922, **44**, 1581.
125. D. Roberts and M. Friedkin, *J. Biol. Chem.*, 1958, **233**, 483.
126. P. A. Shore, A. Burkhalter and V. H. Cohn, Jr., *J. Pharmacol. Exptl. Therap.*, 1959, **127**, 182.
127. G. Olive, M. Lemeignan and P. Lechat, *Ann. Pharm. Franç.*, 1968, **26**, 35.
128. J. A. Ambrose, A. Crimm, J. Burton, K. Paullin and C. Ross, *Clin. Chem.*, 1969, **15**, 361.
129. T. Amano and S. Mizukami, *Yakugaku Zasshi*, 1965, **85**, 1035. *Chem. Abstr.*, 1966, **64**, 8178*a*.
130. C. J. Rogers, C. W. Chambers and N. A. Clarke, *Anal. Biochem.*, 1967, **20**, 321.
131. V. H. Cohn and J. Lyle, *ibid.*, 1966, **14**, 434.
132. S. M. Hess and S. Udenfriend, *J. Pharmacol. Exptl. Therap.*, 1959, **127**, 175.
133. H. D. Dell and R. Kamp, *Archiv der Pharmazie*, 1970, **303**, 785.
134. M. Pesez and P. Poirier, *Méthodes et Réactions de l'Analyse Organique, Vol. III.* Masson, Paris, 1954.
135. G. G. Guilbault, D. N. Kramer and E. Hackley, *Anal. Chem.*, 1967, **39**, 271.
136. G. G. Guilbault, P. Brignac, Jr., and M. Zimmer, *ibid.*, 1968, **40**, 190.
137. G. G. Guilbault, P. J. Brignac, Jr., and M. Juneau, *ibid.*, 1968, **40**, 1256.
138. G. G. Guilbault, S. H. Sadar and R. McQueen, *Anal. Chim. Acta*, 1969, **45**, 1.
139. G. G. Guilbault, S. S. Kuan and P. J. Brignac, Jr., *ibid.*, 1969, **47**, 503.
140. G. G. Guilbault and S. H. Sadar, *Anal. Letters*, 1969, **2**, 41.
141. M. H. Sadar, S. S. Kuan and G. G. Guilbault, *Anal. Chem.*, 1970, **42**, 1770.
142. E. Becquerel, *Ann. Chim. Phys.*, 1871, **27**, 539.
143. G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, 1944, **66**, 2100.
144. R. J. Keirs, R. D. Britt and W. E. Wentworth, *Anal. Chem.*, 1957, **29**, 202.
145. M. Zander, *Angew. Chem., Intern. Ed.*, 1965, **4**, 930.
146. G. Oster, N. Geacintov and A. U. Khan, *Nature*, 1962, **196**, 1089.
147. J. D. Winefordner and P. A. St. John, *Anal. Chem.*, 1963, **35**, 2211.
148. J. D. Winefordner and M. Tin, *Anal. Chim. Acta*, 1964, **31**, 239.
149. R. Zweidinger and J. D. Winefordner, *Anal. Chem.*, 1970, **42**, 639.
150. J. D. Winefordner and H. W. Latz, *ibid.*, 1963, **35**, 1517.

151. J. D. Winefordner and M. Tin, *Anal. Chim. Acta*, 1965, **32**, 64.
152. H. C. Hollifield and J. D. Winefordner, *ibid.*, 1966, **36**, 352.
153. J. D. Winefordner and H. A. Moye, *ibid.*, 1965, **32**, 278.
154. H. A. Moye and J. D. Winefordner, *J. Agr. Food Chem.*, 1965, **13**, 516.
155. W. J. McCarthy and J. D. Winefordner, *J. Assoc. Offic. Agr. Chemists*, 1965, **48**, 915.
156. See ref. (2), p. 179.
157. See ref. (2), p. 185.
158. See ref. (9), p. 243.
159. J. W. Haas, *J. Chem. Educ.*, 1967, **44**, 396.
160. L. Erdey and I. Buzás, *Anal. Chim. Acta*, 1960, **22**, 524.
161. E. H. White, O. Zafiriou, H. H. Kägi and J. H. M. Hill, *J. Am. Chem. Soc.*, 1964, **86**, 940.
162. E. H. White and M. M. Bursey, *ibid.*, 1964, **86**, 941.
163. M. M. Rauhut, A. M. Semsel and B. G. Roberts, *J. Org. Chem.*, 1966, **31**, 2431.
164. A. A. Ponomarenko and B. I. Popov, *Zh. Analit. Khim.*, 1964, **19**, 1397.
165. A. A. Ponomarenko, B. I. Popov, L. M. Amelina, L. V. Grishchenko and R. E. Shindel, *Zh Obshch. Khim.*, 1964, **34**, 4118.
166. A. A. Ponomarenko and L. M. Amelina, *ibid.*, 1965, **35**, 2252.
167. *Idem*, *ibid.*, 1965, **35**, 750.
168. See ref. (9), p. 245.
169. R. L. Bowman and N. Alexander, *Science*, 1966, **154**, 1454.

Talanta, 1972, Vol. 19, pp. 125 to 139. Pergamon Press. Printed in Northern Ireland

ELECTRIFICATION OF GAS BUBBLES AS AN ANALYTICAL TOOL

D. A. PANTONY and D. C. STAGG
Department of Metallurgy, Imperial College of Science and Technology,
Prince Consort Road, London, S.W.7

(*Received* 15 *July* 1971. *Accepted* 2 *October* 1971)

Summary—When a gas passes through a liquid, a charge is produced and this is carried on in the droplets formed when the bubble bursts at the surface of the liquid. A theory to account for the relationship between the bubble charge and concentration of electrolyte, *viz.* $q \propto C^{-1/2}$, is derived and applied to a number of uni-univalent and multivalent electrolytes. The general agreement between theory and experiment and the reasonable reproducibility of the technique show that it could have analytical application. Such use is exemplified in laboratory simulations of flowing systems for continuous analysis and in bubble-charge indication of titration end-points.

IT HAS LONG been known that a gas bubble bursting from an aqueous solution forms droplets that carry a small electrical charge. Indeed, Townsend,[1] by generating a multitude of small bubbles electrolytically and thence a fog of tiny droplets, was able to show that each droplet carried a single electronic charge or a small integral number of such charges. More recently[2] it has been shown that a smaller population of bubbles and droplets carried charges, the sizes of which were appreciable and dependent on bubble radius and on the concentration of an electrolyte in the aqueous phase. The fact that moving colloidal particles, and both ionic and non-ionic liquids passing down a tube cause a current to flow is also well known.[3–5] The mechanism of bursting bubbles and droplet formation has been studied in connection with cloud physics studies[6] where it is known that the liquid cap of the emerging and bursting bubble drains back into the cavity and forms a jet causing ejection of droplets of liquid amounting to about 0·001 of the volume of the original bubble.[7] Mason and Iribarne[2] have proposed a theory to account for the relationship found between bubble charge, q, radius of bubble, r, and ionic concentration, C, namely

$$q = -7 \times 10^3 \, . \, 4\pi r^2 C^{1/2} \exp\{-\tfrac{1}{2} - 10^6 r C^{1/2}/9\}$$

Their experimental results tend to confirm the remarkable relationship between the square root of the ionic concentration and bubble charge, but the mixed terms in the expression make it sensitive to parameters that change the coefficient in the exponential term. In fact, it is possible to show that q becomes proportional to any small power of C under moderate changes of conditions. Nevertheless, the processes could form the basis of a sensitive method of analysis in dilute solution.

An alternative theoretical approach and the results of a systematic analytical investigation are given below.

THEORETICAL APPROACH

Gas bubbles rising through an insulating fluid can readily attain appreciable electrical charges. Present experiments show that these charges can reach between -3 and $+6$ e.s.u per bubble and that, after the bubble has become well detached from its forming orifice, the value is independent of the distance travelled. In the case of doubly distilled water, charges of -3×10^{-3} e.s.u., again independent of distance travelled, are obtained. Evidently the charge is related to the velocity of the bubble and although the movement of the bubble relative to the liquid may tend to cause further charging, the charge dissipates to the liquid if this is at ground potential. A steady state must soon be established between electrical charging and leakage, at least with organic liquids of reasonably high dielectric constant and with aqueous solutions.

In aqueous solution the position is complicated by the possibility of ionic conduction or dissipation of the charge and even in doubly-distilled water charges far less than those in non-conducting media are found, and as the concentration of any electrolyte is increased in the aqueous phase the measured charge decreases still further. Experimental demonstration of such a phenomenon where detector response increases with decreasing concentration is given in Figs. 1 and 2.

The flux of univalent ions causing transfer of charge under a potential gradient $\mathrm{d}E/\mathrm{d}x$ can be expressed as

$$f = \frac{DC}{kT}\frac{\mathrm{d}E}{\mathrm{d}x}$$

where D is diffusivity, C the ionic concentration, k is Boltzmann's constant and T the absolute temperature. But at the gas–liquid interface the distribution of charge will be that of the Gouy double layer. Hence the potential E will be given by

$$E = \frac{4\pi\sigma}{\epsilon\kappa}$$

where σ is the specific surface charge, ϵ the dielectric constant of the solvent and $1/\kappa$ is the measure of the effective double layer thickness irrespective of its type. Hence,

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{4}{\epsilon\kappa} \cdot \frac{\mathrm{d}\sigma}{\mathrm{d}x} = \frac{4\pi}{\epsilon\kappa} \cdot \rho$$

where ρ is the electrical charge density at distance x from the interface.

Substituting for ρ gives

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{-4}{\epsilon\kappa} \,.\, \exp\{-\kappa(x-a)\}$$

where a is the distance of closest approach of the ions to the gas surface.

Hence,

$$f = -\frac{4\pi DC\sigma}{kT\epsilon \exp\{\kappa(x-a)\}} \tag{1}$$

If, under steady state conditions, this is the flux of ions that exactly counterbalances the charging process described above, then it will reach a constant depending only on the velocity of the bubble in a particular medium.

The value of x cannot exceed the thickness, δ, of the film that contributes to the bubble, and accepting the value of κ as $(2C)^{1/2}/4{\cdot}31 \times 10^{-7}\,\mathrm{mm}^{-1}$ for a univalent electrolyte in water at room temperature, then on expanding the exponential term

$$\sigma = -\frac{fkT\epsilon\{\kappa\delta + \kappa^2\delta^2 + \ldots\}}{4\pi DC}$$

The thickness δ is known[2] to be $<10^{-3}$ mm for small ($\sim$0·15 mm radius) bubbles so that, in the range below $C = 10^{-4}M$, the second and later terms of the expansion can be neglected.

Hence,

$$\sigma = -\frac{fk^{1/2}T^{1/2}\epsilon^{1/2}eN^{1/2}\delta}{1000 \times 2^{1/2}\pi^{1/2}DC^{1/2}}$$

Allotting accepted values of Avogadro's number, N, as $6{\cdot}03 \times 10^{23}$, the electronic charge, e, as $4{\cdot}80 \times 10^{-10}$ e.s.u., $\epsilon_{H_2O} = 78{\cdot}6$ at $T = 298°$ K and $k = 1{\cdot}38 \times 10^{-16}$ erg. K^{-1} then $\sigma = -8{\cdot}44 \times 10^{-7} f\delta D^{-1}C^{-1/2}$ e.s.u. or as a charge, $q_{1,1}$, resulting from a bubble of radius r, in a uni-univalent electrolyte,

$$q_{1,1} = -1{\cdot}06 \times 10^{-5} f\delta D^{-1}C^{-1/2}r^2 \text{ e.s.u.}$$

A complementary approach employs the relationship for charge density,

$$\rho = \frac{\epsilon\kappa}{4\pi} \cdot \frac{d\psi}{dx}$$

where ψ is the potential in the double layer. Hence the flux of ions transporting the charge is

$$f = -\frac{DC}{kT} \cdot \frac{4\pi\rho}{\epsilon\kappa}$$

and since

$$\sigma = \int_0^\delta \rho \, dx$$

$$\sigma = -\frac{fkT\epsilon\kappa\delta}{4\pi DC}$$

$$= -8{\cdot}44 \times 10^{-7} f\delta D^{-1}C^{-1/2}$$

Experimental evidence suggests that δ is $\sim$5–10 $\times 10^{-4}$ mm for bubble radii of 0·15–0·3 mm and the flux, expressed as a current density, is about 0·59 e.s.u. cm^{-2}.[2,4] With a typical value of $D = 10^{-3}$ mm^2 sec^{-1} these data give charges per bubble as

$$\sigma = 4\pi r^2 \times 5{\cdot}0 \times 10^{-4}C^{-1/2} \text{ e.s.u.} \tag{2}$$

i.e.,

$$5{\cdot}7 \times 10^{-7}C^{1/2} \text{ e.s.u.} \quad \text{or} \quad 1{\cdot}9 \times 10^{-16}C^{-1/2} \text{ coulomb} \tag{3}$$

The general form of this equation, modified to accommodate different diffusivities and bubble radii is in agreement with results given below.

Mason and Iribarne observed more complex behaviour of charge with respect to bubble radius. This has not been found in the present work although only a small range of bubble sizes has been investigated.

However, these authors found that at electrolyte concentrations above $10^{-4{\cdot}5}M$ their formula for charge was not obeyed; this was also observed in the present work. It seems logical from the proposed theory that charges would be dissipated more efficiently in more concentrated electrolyte solutions, leaving a slight excess of positive ions in the neighbourhood of the bursting bubble to be carried up in the droplet. Reference to the first theoretical approach given in this paper also shows that the first approximation of the expansion of the exponential part of equation (1) is not valid at higher concentrations. Under such conditions the second term becomes significant and the charge should become virtually independent of concentration and fall to quite small values. At higher concentrations, therefore, it would be expected that the charge would fall to a small almost constant value perhaps with a positive sign as is found in practice.

The present state of theoretical treatment of the electrical double layer formed by multivalent ions is inadequate for formulation of a similarly straightforward relationship between charge and electrolyte concentration. If adsorption and flux of a bivalent ion followed the same pattern as that of a univalent ion, then the expression for the charge per bubble would be

$$q_{2,2} = -1{\cdot}49 \times 10^{-5} f \delta D^{-1} C^{-1/2} \text{ esu}$$

However, the double layer appears to be populated with bivalent ions less efficiently than with univalent ions.[8] As a consequence the charge may be smaller than expected and the power to which the concentration is raised is likely to become rather more negative. Presumably, a converse argument could be applied to the counter-ions to explain the similarity of behaviour between uni-bivalent and bi-univalent electrolytes which, in practice, differ only in size of charge and not power in the relationship with concentration.

At the same time, the argument implies that, in a mixture of uni-univalent and bi-bivalent ions the effect of the univalent ions is dominant and equation (2) is likely to hold until bivalent ions are present in considerable excess. Most of these predictions are borne out in practice.

If the process of electrification depended solely on adsorption and double-layer formation it would be expected that different ions, owing to their different surfactant properties, would offer distinctly different bubble charges. A glance at the results for the uni-univalent electrolytes shows that indeed they behave similarly. Moreover, addition of the preferentially adsorbed species should have a dominating effect if adsorption were the single mechanism. In this connection, the effect of non-ionic surfactants is interesting: addition of small quantities of the substances to water causes a marked increase of the negative charge until irreproducibility caused by foaming occurs at approximately $10^{-4}M$, as follows,

Concentration of surfactant, M	Charge per bubble, *esu*
0	$-2{\cdot}9 \times 10^{-3}$
$10^{-6}M$ Nonidet P40	$-1{\cdot}4 \times 10^{-2}$
$10^{-5}M$ Nonidet P40	$-1{\cdot}12$
$0{\cdot}9 \times 10^{-6}M$ Tergitol NPX	$-0{\cdot}303$
$0{\cdot}9 \times 10^{-5}M$ Tergitol NPX	$-7{\cdot}72$

However, the presence of 10^{-6} or $10^{-5}M$ surfactant in experiments with sodium chloride shows that the relationship between concentration of electrolyte and bubble charge, seen in the table above, is affected in terms of size of charge and slightly in terms of slope until the adsorbed surfactant layer becomes so thick in the more concentrated solutions that conduction becomes inefficient.

A ready explanation for the results in pure water lies in the formation of an insulating layer of the organic surfactant at the water-gas interface, thus inhibiting the already weak charge-dissipating effect of the hydronium and hydroxyl ions at their low concentrations. But the presence of an electrolyte again allows charge conduction along a double-layer ion distribution but with a smaller absolute effect. The $q \propto C^{-1/2}$ relationship should therefore still hold, but the negative charge should be larger when the non-ionic surfactant is present. Apart from a slight reduction of the size of the inverse power to which the concentration is raised, these predictions are borne out in practice and confirm that diffusive dissipation of charge is an essential feature of the processes. At the same time, presence of such a non-ionic surfactant makes the method analytically more sensitive provided that too high a concentration of the surfactant is not employed.

TABLE I.—BUBBLE CHARGES IN ORGANIC SOLVENTS

Solvent	Grade	Bubble charge $q \pm s_q$, *esu*
Dimethylformamide	Purified[9]	$+6{\cdot}4 \pm 0{\cdot}1$
Isopentanol	GCR, as supplied	$+2{\cdot}7 \pm 0{\cdot}1$
n-Butanol	GCR, as supplied	$+0{\cdot}38 \pm 0{\cdot}01$
1,4-Dioxan	GCR, as supplied	$-(4{\cdot}1 \pm 0{\cdot}1) \times 10^{-4}$
Dimethylsulphoxide	Commercial, as supplied	$-(1{\cdot}6 \pm 0{\cdot}1) \times 10^{-3}$
Water	Twice distilled	$-(2{\cdot}2 \pm 0{\cdot}1) \times 10^{-3}$
Petroleum ether, 80–100°	A.R., MS treated	$-(3{\cdot}2 \pm 0{\cdot}3) \times 10^{-3}$
Dimethylformamide	GPR, as supplied,	$-(4{\cdot}0 \pm 0{\cdot}2) \times 10^{-3}$
1,4-Dioxan	Karl Fischer grade, as supplied, MS treated	$-(6{\cdot}5 \pm 0{\cdot}1) \times 10^{-3}$
Dimethylsulphoxide	Purified	$-(9{\cdot}5 \pm 0{\cdot}3) \times 10^{-3}$
Benzene	GCR, as supplied, MS treated	$-(1{\cdot}03 \pm 0{\cdot}05) \times 10^{-2}$
Ethyl methyl ketone	GCR, as supplied, MS treated	$-0{\cdot}42 \pm 0{\cdot}02$
Nitrobenzene	AR, as supplied, MS treated	$-1{\cdot}83 \pm 0{\cdot}07$
Pyridine	GPR, anhydrous, as supplied, MS treated	$-3{\cdot}43 \pm 0{\cdot}03$

GCR = Griffin Certified Reagent.
AR = BDH Analytical Reagent Grade.
MS treated = a column of type 5A molecular sieves was included in the closed-circuit flow system.

A rapid survey was made to find the size and sign of charges developed on bubbles rising in organic solvents. Results, given in Table I, must be regarded as preliminary since in most cases no rigorous efforts were made to purify the solvents and in certain cases there was evidence of some solvent attack on the silicone rubber tubing of the apparatus, and no corrections have been made for the small changes of bubble radius due to the different surface tensions. Nevertheless, the wide variation of charge magnitude and its change of sign are noteworthy, and the technique may afford a method for checking purity of organic solvents. In the case of purified dimethylformamide, it was shown that its large positive charge did decrease with increasing concentration of sodium perchlorate but its behaviour was complex and will be the subject of a further communication. No obvious correlation could be found between charge and dielectric constant, donor power, surface tension, dipole moment or viscosity.

RESULTS

The charge per bubble, q, *vs.* concentration, C, relationships for a number of electrolytes are shown in Figs. 1 and 2 and Table II. Clearly, for uni-univalent

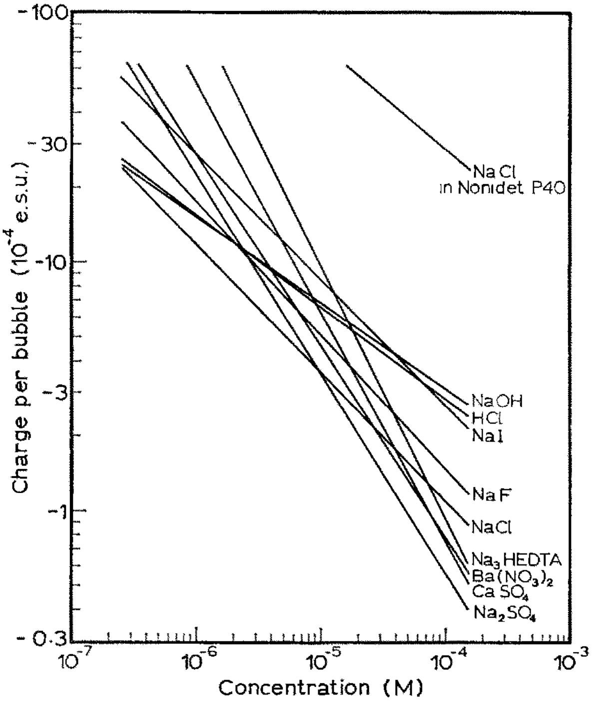


FIG. 1.—Charge-concentration relationships for various electrolytes.

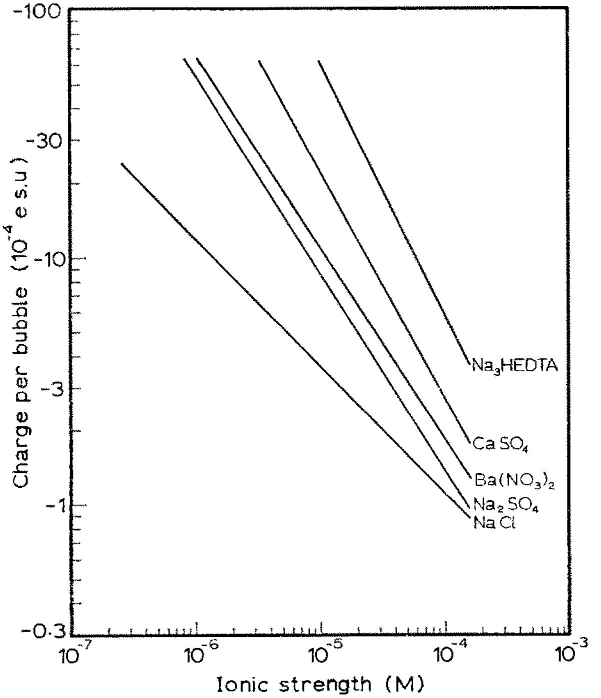


FIG. 2.— Charge-ionic strength relationships for various electrolytes.

TABLE II.—SLOPE AND INTERCEPT, WITH THEIR ERRORS, FOR THE LINE LOG $q = c + m \log C$ FOR VARIOUS ELECTROLYTES, USING 0·1-mm RADIUS BUBBLES

Electrolyte	Atmosphere	The line $\log q = c + m \log C$	
		Slope, $m \pm s_m$	Intercept, $c \pm s_c$
Uni-univalent electrolyte, calculated from (2) and (3)		−0·50	−6·24
NaCl	N_2	−0·52 ± 0·02	−6·01 ± 0·09
NaCl	Air	−0·45 ± 0·02	−5·35 ± 0·08
NaF	N_2	−0·54 ± 0·13	−5·97 ± 0·70
NaI	N_2	−0·51 ± 0·10	−5·59 ± 0·49
NaOH	N_2	−0·35 ± 0·02	−4·90 ± 0·12
HCl	N_2	−0·37 ± 0·01	−5·02 ± 0·06
Na_2SO_4	N_2	−0·80 ± 0·01	−7·44 ± 0·07
Na_2SO_4	Air	−0·67 ± 0·04	−6·57 ± 0·18
$Ba(NO_3)_2$	N_2	−0·77 ± 0·04	−7·16 ± 0·21
$CaSO_4$	N_2	−0·92 ± 0·03	−7·78 ± 0·15
Na_3H-EDTA	N_2	−1·01 ± 0·03	−8·07 ± 0·14
NaCl + $10^{-6}M$ Nonidet P40	Air	−0·42 ± 0·02	−4·21 ± 0·07
NaCl + $10^{-5}M$ Nonidet P40	Air	−0·20 ± 0·01	−1·30 ± 0·05
NaCl + $0·9 \times 10^{-6}M$ Tergitol NPX	Air	−0·44 ± 0·02	−3·25 ± 0·09

TABLE III.—THE LINE LOG $q = c + m \log C$ FOR SODIUM CHLORIDE AND SULPHATE AND CALCIUM SULPHATE IN VARIOUS RATIOS

Ratios of [NaCl]: [Na_2SO_4]	Slope, m	Intercept, c
Pure NaCl	−0·52	−6·01
1:1	−0·52	−6·04
1:5	−0·52	−6·31
1:10	−0·61	−6·78
Pure Na_2SO_4	−0·80	−7·44
Ratios of [NaCl]: [$CaSO_4$]		
Pure NaCl	−0·52	−6·01
1:1	−0·66	−6·75
1:5	−0·71	−6·92
1:10	−0·86	−7·47
Pure $CaSO_4$	−0·92	−7·78

electrolytes the $q \propto C^{-1/2}$ relationship holds well and predicted values for the charge are in reasonable agreement with experimental values, and incidentally, with those of Mason and Iribarne.[2] For multivalent electrolytes, illustrated by sodium sulphate, barium nitrate, calcium sulphate and the sodium salt of EDTA at pH 8, the power to which the concentration should be raised increases until almost a reciprocal relationship between charge and concentration holds. Mixtures of sodium sulphate and sodium chloride and of calcium sulphate and sodium chloride give intermediate values of the index, weighted towards one half, until the bivalent ion is in large excess, as shown in Table III.

It appears that the theory proposed above is essentially substantiated. The technique and results provide a novel method of analysis of dilute electrolyte solutions. There are two outstanding features that make the method attractive, based on the proportionality between detector response and the reciprocal of a power of electrolyte concentration. This gives an increasing signal with decreasing concentration, a property not found in other techniques. In practice the square-root relationship does not detract substantially from the sensitivity, and in the case of multivalent electrolytes where the function is almost reciprocal there is virtually no loss of sensitivity. Thus, sensitivity and precision, expressed as relative error, improve with decreasing concentration and the lower limit is set by the ionization of the solvent.

Hence concentrations of uni-univalent electrolytes, singly or in mixtures, can be measured by reference to equations (2) and (3) or to the straight line plots of log q *vs.* log C or to the parabolic curves of q *vs.* C. Since the equations analogous to (2) are not yet predictable for multivalent electrolytes, reference to calibration curves is necessary for their analysis. For many purposes mixtures of univalent and multivalent ions can be analysed with adequate precision in terms of concentration or ionic strength by using a calibration curve, especially when the univalent kind is not in proportionally minor concentration.

In the case of a method that yields a greater detector response with decreasing concentration and is highly sensitive to changes of ionic strength, one obvious application is in detection of titrimetric end-points. Figures 3–8 illustrate its usefulness

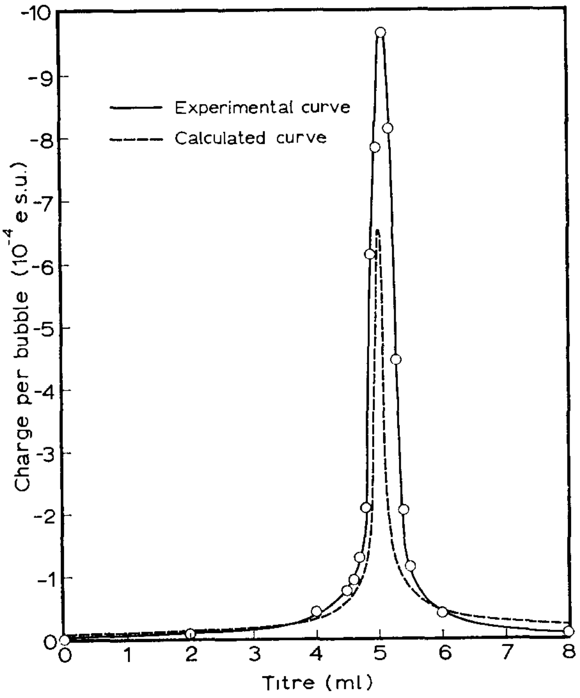


FIG. 3.—Titration of 250 ml of $10^{-3}M$ sulphuric acid with 0·05M barium hydroxide.

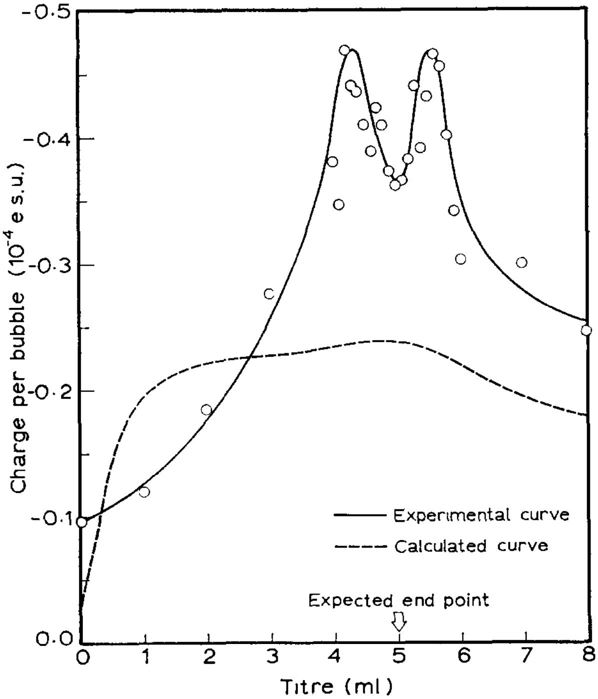


FIG. 4.—Titration of 250 ml of $10^{-3}M$ sodium sulphate with $0{\cdot}05M$ barium chloride.

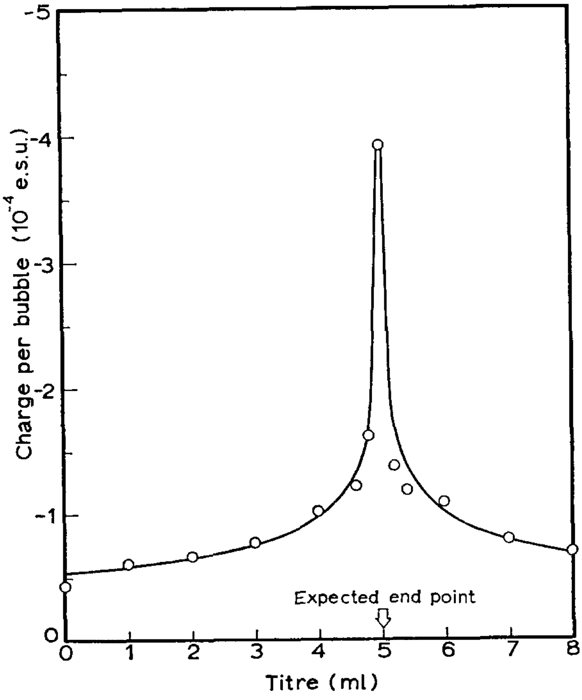


FIG. 5.—Titration of 250 ml of $10^{-3}M$ acetic acid with $0{\cdot}05M$ sodium hydroxide.

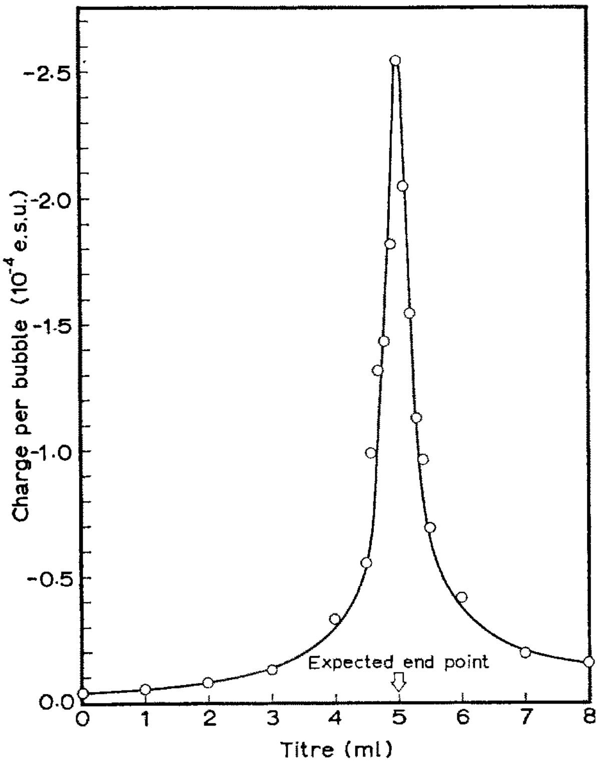


FIG. 6.—Titration of 250 ml of $10^{-3}M$ acetic acid with 0·05M ammonia.

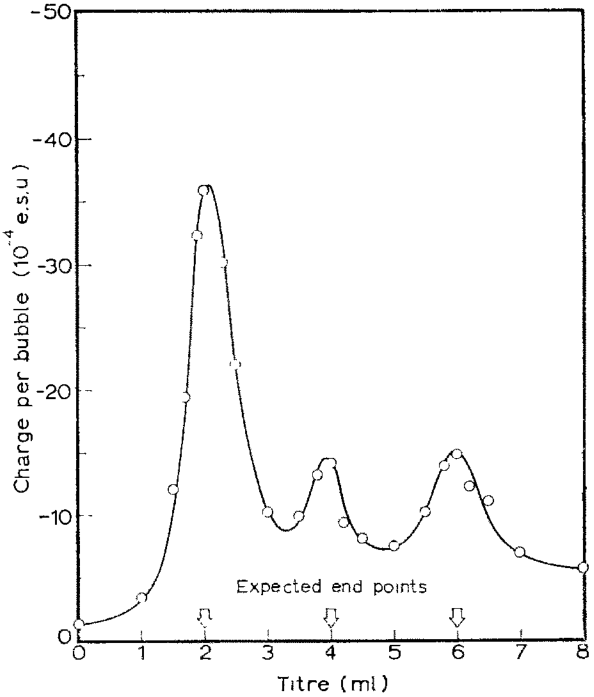


FIG. 7.—Titration of 200 ml of $10^{-3}M$ *ortho*phosphoric acid with 0·1M sodium hydroxide.

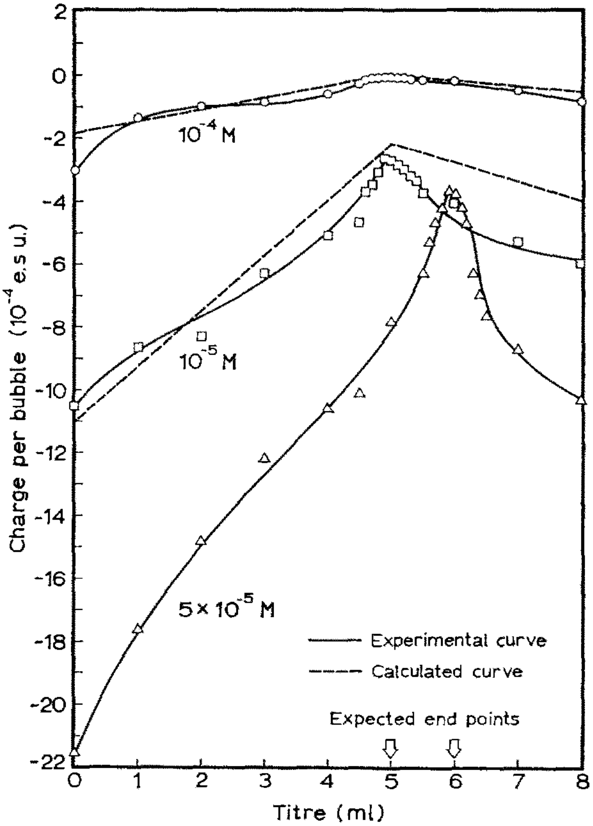


FIG. 8.—Titration of various concentrations of nickel with suitable concentrations of EDTA at pH 8.

in the following titration reactions:

$$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2H_2O$$

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$

$$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$$

$$NH_4OH + CH_3COOH \rightarrow CH_3COONH_4 + H_2O$$

$$H_3PO_4 \xrightarrow{OH^-} H_2PO_4^- + H_2O \xrightarrow{OH^-} HPO_4^{2-} + 2H_2O \xrightarrow{OH^-} PO_4^{3-} + 3H_2O$$

$$Ni^{2+} + HY^{3-} \rightarrow NiY^{2-} + H^+ \ (pH \sim 8, Y = \text{EDTA ion})$$

These cover a wide range of changes of ionic strength during the course of a titration and in some cases the changes are extremely small. Nevertheless, the end-points occur at the expected values and are indicated with a clarity that is remarkable at $10^{-3}M$ concentrations and in some cases becomes even better at lower concentrations. End-points shown by analogous potentiometric methods are barely discernible even at the highest concentrations examined. It will be seen from Figs. 3 and 8 that the bubble-charge curves follow those calculated from calibration curves such as those shown in Figs. 1 and 2 with the exception of that for the precipitation of barium sulphate from barium chloride and sodium sulphate shown in Fig. 4. This displays a most remarkable shape and, while at the end-point the bubble charge tends towards that to be expected from solubility product, concentration of other ions and the charge/concentration relationships, the charges found on either side of the equivalence point are far larger than those expected. The results are the same if a filter is inserted in the liquid circuit. These observations imply that before and after the end-point the ionic concentrations of free ions are far smaller than those expected from thermodynamic and stoichiometric relationships. It would appear that adsorption on the almost colloidal barium sulphate and on the aging precipitate withdraws a great many ions from solution and that the technique offers a method of following nucleation, precipitation and adsorption processes.

EXPERIMENTAL

The apparatus, built essentially of Perspex and high density polythene, is illustrated in Figs. 9 and 10. The second kind is essentially that designed by Mason and Iribarne[3] and is particularly useful if control of gas atmosphere and prevention of dust contamination are required. Details of screening and earthing are important. However, a comparison between the apparatus using nitrogen and laboratory air atmospheres showed that they gave identical results.

The bubble charges were measured as a current on a Keithley Electrometer, type 602, by connecting the collecting funnel *A* to the solution *via* the screening at *B* and *via* a triaxial/coaxial adapter. Liquid was kept flowing to spill over the circular weir *C*, either fed from a large reservoir by gravity, thus simulating a continuous stream and providing a constantly renewed liquid surface, or by closed circuit peristaltic pumping with a Watson-Marlow type MHRE pump. The second system was of particular application in the bubble-charge titrations. A balance must be arranged between the inflow of gas as bubbles plus that entering at *E* and the withdrawal at the exit tube *F*. Rates of bubble generation were measured with a photoelectric device coupled to an Advance Instruments

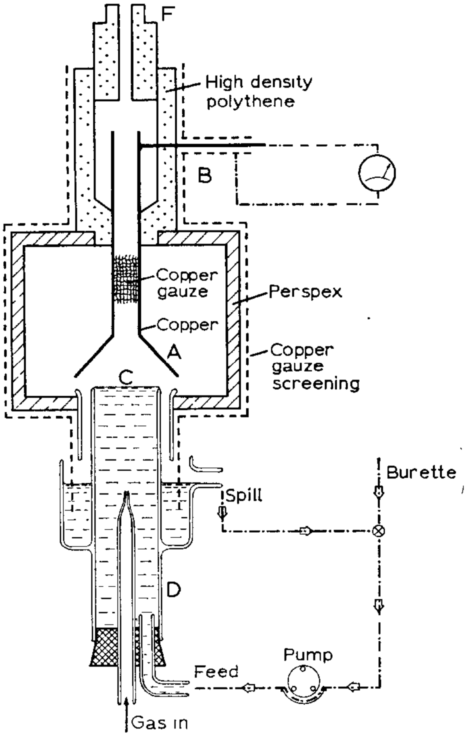


FIG. 9.—First bubble-chamber apparatus.

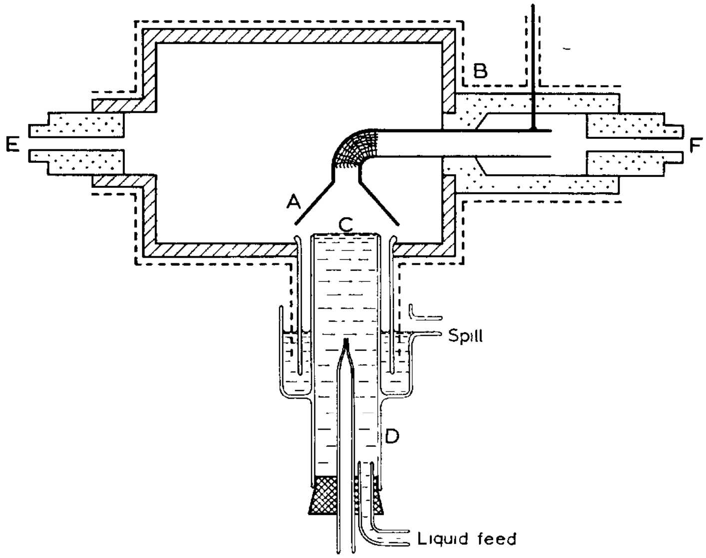


Fig. 10.—Second bubble-chamber apparatus.

Timer, type TC12A. In the present series of experiments the bubble-rate control was crude and was contrived by adjustment of the usual valve fittings on a nitrogen cylinder: undoubtedly this could be improved to some advantage but it was quite adequate for these experiments, the relative fluctuation in bubble rate being less than ±10%.

The current measured on the electrometer was converted into individual bubble charges from the

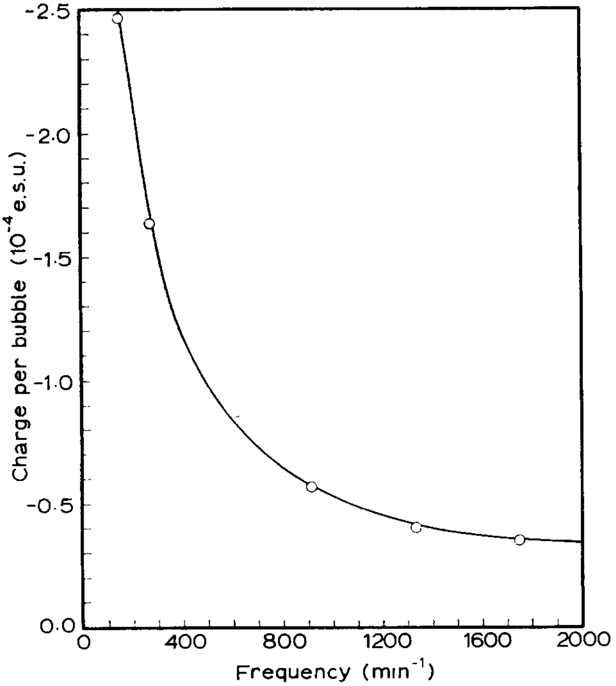


Fig. 11.—Effect of bubble frequency on charge per bubble in $10^{-5}M$ sodium chloride and with 0·1-mm radius bubbles.

measured bubble rate, which had been selected from previous experimentation. Lower bubble rates had the disadvantage that, while the bubble charges were larger, the electrometer needle oscillated wildly at the bubble bursting stage and, at the same time, results were of rather poor reproducibility. A plot of bubble charge against bubble rate is shown in Fig. 11 and most measurements were conducted at rates of 1000–1200 bubbles/min, where changes of rate had smaller effects. This procedure also had the advantage that meter readings became meaningful and the occasional spurious low currents, apparently caused by a bubble brushing against the glass wall of the flow tube *D* during upward traverse, became obvious and could be ignored. This charge-deficiency problem may set a lower limit to the solution capacity of the apparatus because a narrower tube *D* suffers more seriously from this disadvantage. Inclusive of small reservoirs and any molecular-sieve drying tubes, the capacity of the closed circuit system was about 250 ml in the apparatus used in the majority of this work.

Preliminary experiments established that over the practical bubble-paths available (60–150 mm) the distance traversed by a bubble in water or organic solvents had no effect on the bubble charge, and the rate of flow of liquid similarly had no significant effect, provided that it exceeded 50 ml/min. Bubble velocities were found to be reproducible in both designs of apparatus and in long columns of the liquids investigated, namely, for water 0·333 ± 0·046 m/sec and for dimethylformamide, 0·220 ± 0·008 m/sec. The lowering of charge observed when a bubble brushed the side of the tube was presumably to be attributed to a slowing down, to an increased dissipation of charge and perhaps to a disturbing of the double layer.

CONCLUSIONS

The electrification of gas bubbles affords a simple and comparatively inexpensive means of analysis of dilute solutions. The proposed theory is confirmed in practice and from the resulting formula it is possible to evaluate concentrations of electrolytes. The sensitivity and usefulness of the technique is demonstrated by the application to identification of titrimetric end-points and to analysis of continuously flowing solutions. Considerable extension of the applications seems possible in double layer, diffusion and analytical fields and work on continuous and titrimetric analysis is continuing.

Acknowledgements—The authors express their thanks to the Central Electricity Generating Board for financial support, including a bursary, for this work. Shell Chemicals kindly provided the Nonidet P40, and B.D.H. the Tergitol NPX.

Zusammenfassung—Wenn ein Gas durch eine Flüssigkeit strömt, bildet sich eine Ladung; diese geht in die Tröpfchen über, die beim Platzen der Blase an der Flüssigkeitsoberfläche entstehen. Eine Theorie wird abgeleitet, die die Beziehung zwischen Blasenladung und Elektrolytkonzentration beschreibt, nämlich $q \propto C^{1/2}$, und auf eine Anzahl ein-einwertiger und mehrwertiger Elektrolyte angewandt. Die allgemeine Übereinstimmung zwischen Theorie und Experiment und die zufriedenstellende Reproduzierbarkeit des Verfahrens zeigen, daß es analytisch angewandt werden könnte. Das wird an Beispielen gezeigt, wie simulierten fließenden Systemen zur kontinuierlichen Analyse und der Anzeige von Titrationsendpunkten mit Hilfe der Blasenladung.

Résumé—Lorsqu'un gaz passe à travers un liquide, il se produit une charge qui est transportée dans les gouttelettes formées lorsque la bulle éclate à la surface du liquide. Une théorie est établie pour rendre compte de la relation entre la charge de la bulle et la concentration de l'électrolyte, c'est-à-dire $q \propto \mathrm{C}^{-1/2}$, et appliquée à un certain nombre d'électrolytes mono-monovalents et multivalents. L'accord général entre la théorie et l'expérience et la reproductibilité raisonnable de la technique montre qu'elle peut avoir des applications analytiques. Un tel emploi est illustré par les simulations en laboratoire de systèmes en écoulement pour l'analyse en continu et par l'indication de points de fin de titrage par charge de bulle.

REFERENCES

1. J. S. Townsend, *Phil. Mag.*, 1898, **45**, 125.
2. J. V. Iribarne and B. J. Mason, *Trans. Faraday Soc.*, 1967, **63**, 2234.
3. H. R. Kruyt, ed., *Colloid Science*, Vol. I, p. 221. Elsevier, Amsterdam, 1952.
4. W. F. Cooper, *Brit. J. Appl. Phys., Suppl.* No. 2, 1953, S11.
5. H. N. Keller and H. E. Hoelscher, *Ind. Eng. Chem.*, 1957, **49**, 1433.
6. D. C. Blanchard, *Progr. Oceanog.*, 1963, **1**, 71.
7. D. M. Newitt, N. Dombrowski and F. H. Knelman, *Trans. Inst. Chem. Eng.*, 1954, **32**, 244.
8. P. Delahay, *Double Layer and Electrode Kinetics*, p. 48. Interscience, New York, 1965.
9. G. P. Kumar and D. A. Pantony, *Proc. 3rd. Intern. Congr. Polarography* (*Polarography*, **1964**), 1964, 1061.

Talanta, 1972, Vol. 19, pp. 141 to 146. Pergamon Press. Printed in Northern Ireland

TITRIMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF MANGANESE AFTER AMPLIFICATION

J. W. HAMYA and A. TOWNSHEND
Chemistry Department, Birmingham University, P.O. Box 363, Birmingham 15, England

(*Received* 17 *August* 1971. *Accepted* 21 *September* 1971)

Summary—Manganese (5–100 μg) is oxidized to permanganate by periodate in 3 or 6% nitric acid. After masking of the excess of periodate with molybdate the permanganate and iodate formed are titrated iodimetrically.

MANGANESE is conveniently determined titrimetrically after oxidation to permanganate. Various oxidants have been recommended. Sodium bismuthate[1,2] and lead(IV) oxide[3] give rapid oxidation, but the excess of reagent has to be filtered off before titration of the permanganate. Silver(II) oxide,[4] dissolved in cold nitric, perchloric or sulphuric acid also gives complete and rapid oxidation at room temperature, and the excess of silver(II) ions is completely destroyed by dilution and warming for a few minutes. Peroxydisulphate ions[5] are very effective with silver ions acting as a catalyst; the addition of phosphoric acid[6,7] has been suggested to prevent precipitation of manganese dioxide. The excess of oxidant is destroyed by prolonged boiling. Decomposition of permanganate at this stage is retarded by buffering the solution with disodium hydrogen phosphate, and keeping the boiling period as short as possible.[8] In all these methods, the permanganate may be determined titrimetrically, after removal of the excess of added oxidant, by using for example arsenic(III)[9] or iron(II) sulphate.

Willard and Greathouse[10] used periodate to oxidize manganese to permanganate:

$$2Mn^{2+} + 5IO_4^- + 3H_2O \rightarrow 2MnO_4^- + 5IO_3^- + 6H^+ \qquad (1)$$

The permanganate formed was measured colorimetrically. Attempts to apply a titrimetric finish have been hampered by the presence of periodate and iodate, both of which are also strong oxidants, and would interfere in the permanganate titration. Attempts to remove iodate and periodate by precipitation with mercury did not give satisfactory results.[11] Recently, it was found that periodate can be masked by molybdate, whereas iodate is unaffected.[12] In particular, this masking effect was used to achieve a 24-fold amplification for iodide, based on the reaction:

$$I^- + 3IO_4^- \rightarrow 4IO_3^-$$

The iodate formed could be determined iodimetrically, a titrimetric[13] or spectrophotometric[14] finish being used after masking of the excess of periodate. It seemed probable that the same masking effect could be utilized in the determination of permanganate formed by periodate oxidation of manganese(II). In this instance, the products of reaction (1) are reacted with iodide:

$$2MnO_4^- + 10\,I^- + 16H^+ \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O \qquad (2)$$

$$5IO_3^- + 25I^- + 30\,H^+ \rightarrow 15I_2 + 15H_2O \qquad (3)$$

whereas the excess of periodate is masked by molybdate. As the amount of iodate formed in the reaction is stoichiometrically related to the amount of manganese present initially, the overall production of iodine can be represented by:

$$2Mn^{2+} \equiv 20\ I_2$$

Titration of the iodine produced gives an appreciable amplification of the manganese. The present paper describes the development of this amplification procedure.

EXPERIMENTAL

Aqueous solutions

All chemicals used were analytical reagent grade.

Potassium metaperiodate. Recrystallized from water and vacuum-dried in the dark. Dissolve 1·400 g in small portions of hot water and after cooling make up to 500 ml with water. Store in a dark glass bottle.

Manganese(II) nitrate solution. To contain 98·66 μg of manganese per ml.

Nitric acid (30%). Dilute 30 ml of conc. acid to 100 ml. Boil gently for 2 min, cool and store in a dark glass bottle.

Potassium carbonate solution, 30%.

Ammonium molybdate solution, 12·5%. Freshly prepared.

Potassium iodide solution, 10%. Freshly prepared.

Acetate buffer. Freshly prepared from 0·2M sodium acetate and glacial acetic acid to give a pH of 2.

Sodium thiosulphate solution, $2 \times 10^{-3}M$.

Procedure for determination of manganese (5–100 μg)

To the sample containing $<50\ \mu$g of manganese in a 10-ml graduated flask, add 1 ml of 30% nitric acid (2 ml for $>50\ \mu$g of manganese) and 2 ml of periodate solution and make up to the mark with distilled water. Hold down the stopper with plastic-covered wire and, after gentle mixing, lower the flask carefully into boiling water and leave for 30 min. Cool the reaction mixture, transfer it, with washing, to a conical flask, and add 1·5 ml (or 3 ml when 2 ml of acid were added) of 30% potassium carbonate solution, 5 ml of molybdate solution and 10 ml of buffer solution. Add 2·5 ml of 10% potassium iodide solution, allow to stand for about 2 min and titrate with $2 \times 10^{-3}M$ sodium thiosulphate, adding Thyodene as indicator near the end-point. Take a blank of distilled water through the whole process.

DISCUSSION

The periodate oxidation of manganese

The reaction between manganese(II) and periodate ions was studied by some early workers[15–18] with conflicting results, but Willard and Greathouse were the first to use it as the basis of a colorimetric method for the quantitative determination of manganese. Originally it was applied to the determination of manganese in steels and iron ores. Later its use was successfully extended, often with some modifications, to water,[19] to animal and vegetable materials[20–22] and to salt solutions.[23]

Willard and Greathouse emphasized the danger of having insufficient acid in the reaction mixture; and they stated that a very large concentration of acid does no harm to the development of the permanganate colour. However, the smallest amount of manganese they determined was 2·5 mg per 100 ml of solution. Richards[21] pointed out that if the amount of manganese present is very small, for example 5 μg or less, the danger lies in excessive acidity rather than in its insufficiency. He found that 15% sulphuric acid was sufficient to prevent full colour development or to cause it to fade rather rapidly, the solution gradually assuming a yellow tint.

The acids that have been used include nitric, sulphuric and phosphoric acids or any mixture of them. Hydrochloric acid is not recommended because chloride is oxidized by periodate and thus would interfere. Perchloric acid appears to prevent the oxidation of some manganese(II) and apart from its use in kinetic studies, has never come into general use.

Clark,[23] in determining manganese in salt solutions, preferred phosphoric acid as he found it more satisfactory than other acids for the rapid development of the permanganate colour. He used solutions at about pH 2 and states that a difference of 1 μg of manganese in 50 ml of solution can be observed, if Nessler tubes are used. Phosphoric acid is thought to play a role as a complexing agent for manganese(III) and manganese(IV). Richards found that for 25–500 μg of manganese, the rate of oxidation was a minimum in 9–10% sulphuric acid. With below 1% acid the colour developed very rapidly but the solutions showed the same yellow tint and tendency to rapid fading as are found when the acidity is too great. He recommended the use of 5–6% acid, unless manganese was present in very considerable amounts to justify the use of 15–20% acid, and applied the method to the colorimetric determination of very small amounts of manganese in certain biological materials.

These contradictory results led to investigations of the kinetics and mechanism of the formation of permanganate from manganese(II) by periodate in nitric, sulphuric and perchloric acid media.[24,25] The reaction was found to be autocatalytic, with an induction period, and its rate was proportional to the concentrations of manganese(II) and periodate and also increased with permanganate concentration. In perchloric acid, a violet manganese(III) complex is formed as an intermediate. The proposed mechanism may be represented as:

$$2\mathrm{Mn(II)} + \mathrm{IO_4^-} \xrightarrow{\text{slow}} 2\mathrm{Mn(III)} + \mathrm{IO_3^-} \tag{4}$$

$$\mathrm{Mn(III)} + 2\mathrm{IO_4^-} \longrightarrow \mathrm{MnO_4^-} + 2\mathrm{IO_3^-} \tag{5}$$

$$\mathrm{Mn(II)} + \mathrm{MnO_4^-} \longrightarrow \mathrm{Mn(III)} + \mathrm{MnO_4^{2-}} \tag{6}$$

$$\mathrm{Mn(II)} + \mathrm{MnO_4^{2-}} \longrightarrow 2\mathrm{Mn(IV)} \tag{7}$$

$$\mathrm{Mn(IV)} + \mathrm{Mn(II)} \longrightarrow 2\mathrm{Mn(III)} \tag{8}$$

In particular, the reactions show that manganese(IV) cannot be oxidized unless it is first reduced by manganese(II) [reaction (8)]. Thus some manganese may be trapped as manganese(IV), if its concentration ever exceeds that of manganese(II).

Establishment of optimal conditions

In the present work attempts were made to oxidize manganese(II) between pH 5 and 8, as it was thought that the reaction might be faster than at higher acidities. It was observed, however, that although permanganate was formed more or less instantaneously, there followed the formation of a permanent brown precipitate or colloidal suspension of manganese(IV) oxide [reaction (7)]. At pH 7–8, also, the titration volumes were always 20% greater than theoretical. It was clear that to avoid the permanent formation of manganese(IV), the mixture of periodate and manganese had to be optimally acidified.

The oxidation of 100 μg of manganese was investigated, using nitric, perchloric and sulphuric acids at different concentrations. Phosphoric acid was not used because the formation of phosphomolybdate in the final titration step is undesirable because of its colour and the rapid production of molybdenum blue. Sulphuric acid gave variable results, although this is the acid which most workers have used in this reaction. The permanganate colour developed quite slowly, especially in 3–9% acid. At acidities below 1% sulphuric acid, a brown colloidal suspension was produced. Nitric and perchloric acids were preferable to sulphuric acid; spectrophotometric measurements showed that nitric acid led to the stoichiometric formation of permanganate more rapidly than did perchloric acid. After oxidation in 6% nitric acid, 25–450 μg of manganese could be determined spectrophotometrically as permanganate at 525 nm. The calibration graph was rectilinear and comparable to that of standard amounts of permanganate in the presence of periodate and nitric acid at similar concentrations, showing that oxidation was stoichiometric. At this acidity, however, <25 μg of manganese required more than 30 min heating for complete oxidation. Lowering the acidity to 3% markedly improved the reaction rate and samples containing up to 100 μg of manganese could be quantitatively oxidized within 30 min, although for >50 μg of manganese the use of 6% acid gave a faster reaction. If the nitric acid contained nitrogen oxides little or no reaction took place, but nitrogen oxides were readily eliminated by boiling the acid before use.

The effect of periodate concentration on the rate and extent of reaction was much less pronounced than that of acidity, provided there was sufficient periodate present. Theoretically, 10·47 mg of potassium periodate are required to oxidize one mmole of manganese. Many early investigators used far greater excesses of solid periodates for the reaction than was necessary, and some workers[26,27] used silver salts as catalysts, so as to permit the use of less periodate. High,[28] using periodate dissolved in 0·5% nitric acid, found that as little as 50 mg of periodate sufficed for the oxidation of 2·3 mg of manganese 100 ml of solution. The oxidation was as rapid with this concentration of periodate as when larger amounts of a solid periodate were used. In the present work it was found that 5·6 mg of potassium periodate in 10 ml of aqueous solution is suitable for a wide range of manganese concentrations.

After quantitative oxidation of manganese to permanganate, the excess of periodate is masked by molybdate, iodide is added, and the iodine formed [reactions (2) and (3)] is titrated with thiosulphate solution. As little as 5 μg of manganese could be determined in this way. The results for the determination of 5–100 μg of manganese are summarized in Table I. The blank titration was 0·3–0·6 ml. Alternatively, the permanganate colour may be monitored by the established spectrophotometric procedure.

The induction period was not constant for apparently identical reaction mixtures, but was generally 3–5 min from the initial insertion of the reaction flask in the boiling water-bath. Methods for shortening the induction period have been suggested, for example, the use of a few μg of manganese dioxide and smooth metallic platinum or the use of small amounts of iodate and permanganate,[25] but such expedients were found to be unnecessary. Very small amounts of certain reductants such as nitrite, sulphite and hydrogen peroxide lengthen the induction period although the concentration of the reductant must exceed that of the manganese before the effect is appreciable. However, reductants consume periodate, and therefore interfere by giving a positive error. Many metals form iodates or periodates which are insoluble in dilute acids. However, addition of up to 100 μg of aluminium, antimony(III), silver, lead, bismuth, barium, calcium, magnesium, mercury(II), zinc, tin(II), iron(III), lithium or zirconium

TABLE I.—TITRIMETRIC DETERMINATION OF MANGANESE(II) AFTER AMPLIFICATION

Manganese taken, μg	Nitric acid used, %	Number of determinations	Mean recovery, %	Standard deviation, %
100*	6	10	$100{\cdot}1_8$	$0{\cdot}7_8$
50	6	6	$101{\cdot}5_2$	$0{\cdot}8_4$
25	6	6	$99{\cdot}8_5$	$1{\cdot}5_2$
50	3	5	$100{\cdot}2_3$	$1{\cdot}2_4$
25	3	4	101·0	$1{\cdot}0_7$
20	3	5	$100{\cdot}2_3$	1·0
10	3	5	$100{\cdot}6_4$	1·9
5	3	8	$100{\cdot}2_2$	4·2

* 20 ml of $2 \times 10^{-3}M$ sodium thiosulphate solution required.

to the reaction mixtures had no deleterious effect on the determination of 100 μg of manganese. Cobalt(II) and nickel gave a hue that interfered with the colour change at the end-point of the final titration. Although the effects of halide and organic anions were not examined, these would undoubtedly be oxidized by periodate, but could be eliminated by wet ashing with acids.

The determination of 5–100 μg of manganese is readily achieved by utilizing the amplification resulting from the stoichiometric formation of 5 iodate ions for every 2 permanganate ions formed. Such a procedure is made possible by the masking of excess of periodate by molybdate. This amplification procedure should be of general application to all species that are oxidized by periodate to give an oxidizing species and iodate ions, for example:

$$2Cr^{3+} + 3IO_4^- + 4H_2O \rightarrow Cr_2O_7^{2-} + 3IO_3^- + 8H^+.$$

Acknowledgement—The authors thank Professor R. Belcher for his interest and encouragement. J. W. Hamya thanks the Association of Commonwealth Universities for a Commonwealth Scholarship, and the Uganda Government for study leave.

Zusammenfassung—Mangan (5–100 μg) wird mit Perjodat in 3 oder 6% Salpetersäure zu Permanganat oxidiert. Nach Maskierung des überschüssigen Perjodats mit Molybdat wird das gebildete Permanganat und Jodat jodometrisch titriert.

Résumé—On oxyde le manganèse (5–100 μg) en permanganate par le periodate en acide nitrique à 3 ou 6%. Après dissimulation de l'excès de periodate par le molybdate, le permanganate et l'iodate formé sont titrés par iodométrie.

REFERENCES

1. W. Blum, *J. Am. Chem. Soc.*, 1912, **34**, 1379.
2. G. E. F. Lundell, *ibid.*, 1923, **45**, 2600.
3. I. M. Kolthoff and J. I. Watters, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 8.
4. J. J. Lingane, and D. G. Davis, *Anal. Chim. Acta*, 1956, **15**, 201.
5. H. Marshall, *Chem. News*, 1901, **83**, 76.
6. H. A. Bright and C. P. Larrabee, *J. Res. Natl. Bur. Stds.*, 1929, **3**, 573.
7. R. Lang and F. Kortz, *Z. Anal. Chem.*, 1931, **85**, 181.
8. H. D. Hillson, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 560.
9. K. Gleu, *Z. Anal. Chem.*, 1933, **95**, 305.
10. H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, 1917, **39**, 2366.
11. H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 399.
12. D. Burnel, *Compt. Rend.*, 1965, **261**, 1982.

13. R. Belcher, J. W. Hamya and A. Townshend, *Anal. Chim. Acta*, 1970, **49**, 570.
14. *Idem*, *Chim. Anal. (Bucharest)*, 1971, **1**, 23.
15. S. R. Benedict, *Am. Chem. J.*, 1905, **34**, 581.
16. M. Langlois, *Ann. Chim. Phys.*, 1852, **34**, 257.
17. C. Rammelsberg, *Ann. Phys. Chem.*, 1868, **134**, 528.
18. W. B. Price, *Am. Chem. J.*, 1903, **30**, 182.
19. E. Barton and H. Thompson, *Proc. Iowa Acad. Sci.*, 1929, **36**, 245.
20. J. T. Skinner and W. H. Peterson, *J. Biol. Chem.*, 1930, **88**, 1930.
21. M. B. Richards, *Analyst*, 1930, **55**, 554.
22. J. Davidson and R. G. Capen, *J. Assoc. Offic. Agr. Chem.*, 1929, **12**, 310; 1931, **14**, 547.
23. N. A. Clark, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 241.
24. J. D. H. Strickland and G. Spicer, *Anal. Chim. Acta*, 1949, **3**, 517.
25. G. R. Waterbury, A. M. Hayes and D. S. Martin, *J. Am. Chem. Soc.*, 1952, **74**, 15.
26. F. Nydahl, *Anal. Chim. Acta*, 1949, **3**, 144.
27. F. Koroleff, *Acta. Chem. Scand.*, 1947, **1**, 503.
28. J. H. High, *Analyst*, 1943, **68**, 368.

Talanta, 1972, Vol. 19, pp. 147 to 155. Pergamon Press. Printed in Northern Ireland

APPLICATION DES METHODES COULOMETRIQUES AUX DOSAGES MICROANALYTIQUES DU MANGANESE ET DU CHROME DANS LES COMPOSES ORGANIQUES

M. BIGOIS
(avec la collaboration technique de M. MARCHAND)
Service Central de Microanalyse du Centre National de la Recherche Scientifique,
2, rue Henry Dunant, 94—Thiais, France

(*Reçu le* 12 *juillet* 1971. *Accepté le* 24 *août* 1971)

Résumé—La coulométrie à intensité constante est appliquée à la détermination microanalytique du manganèse et du chrome contenus dans les substances organiques après minéralisation appropriée. Les substances sont décomposées par un mélange d'acides sulfurique et nitrique. Le manganèse et le chrome sont respectivement oxydés en ions permanganiques par le persulfate d'ammonium, et en ions bichromiques par l'acide perchlorique. Les ions MnO_4^- et $Cr_2O_7^{2-}$ sont titrés par les ions Fe^{2+} formés électrolytiquement à courant constant à partir d'ions Fe^{3+} contenus dans la solution avec une fin de titrage ampérométrique.

LES HETEROELEMENTS rencontrés dans les molécules organiques sont de plus en plus nombreux et divers et, corrélativement, les problèmes de leurs dosages microanalytiques se posent à notre Service. Pour les résoudre, les méthodes appliquées, à cette èchelle, doivent être non seulement précises et rapides, mais également aussi sélectives que possible, ce qui élimine, entre autres, le recours à la gravimétrie classique d'oxydes et de sulfates (*cf.* Réf. 1).

Sous réserve de la comparer ultérieurement à d'autres méthodes de mesures finales susceptibles d'être mises en oeuvre, tant classiques (titrimétrie complexométrique) que modernes (spectrométrie de flamme, spectrométrie d'absorption atomique *etc.*), la méthode fondée sur la génération électrolytique des ions titrants et leur mesure coulométrique nous a semblé réunir les qualités requises.

En effet nous appliquons un principe classique de minéralisation préalable de la substance organique qui comporte une attaque sulfonitrique puis, si nécessaire, une oxydation des ions porteurs de l'élément à doser et qui peut être sélective; elle permet d'obtenir une espèce ionique unique dans laquelle cet élément possède une valence définie; il est alors possible de doser cette espèce ionique par des ions ou molécules appropriés, réducteurs ou oxydants, engendrés in situ par électrolyse de la solution et mesurés par coulométrie, dans des conditions qui peuvent également être sélectives.

L'ensemble de ces réactions d'oxydoréduction chimiques et électrochimiques peut conférer à la méthode un caractère de spécificité permettant de résoudre avec précision des problèmes d'analyse particuliers.

Les méthodes de dosages de métaux comportant un titrage coulométrique ont déjà donné lieu à de nombreuses publications, dans le cadre de l'analyse minérale, et notamment en vue du dosage du manganèse et du chrome dans les aciers.[2,3] Le présent travail a pour objet l'adaptation de ces méthodes aux dosages microanalytiques du manganèse et du chrome dans les composés organiques.

Les principes des titrages électrochimiques mis en oeuvre sont classiques et décrits dans les ouvrages généraux; il convient cependant de les rappeler brièvement.

L'attaque sulfonitrique initiale du prélèvement analytique fournit en solution des ions manganeux Mn^{2+} et chromique Cr^{3+}; leur titrage électrochimique exige leur oxydation préalable en ions permanganiques MnO_4^- et bichromiques $Cr_2O_7^{2-}$. Les réactifs oxydants utilisés à cette fin sont respectivement le persulfate d'ammonium,[2,3] dans le premier cas, et l'acide perchlorique[4] dans le second. Les ions MnO_4^- et $Cr_2O_7^{2-}$ sont titrés par des ions ferreux Fe^{2+} engendrés par électrolyse d'une solution d'ions ferriques Fe^{3+}, en milieu acide; le point final de titrage qui correspond à l'apparition d'un excès d'ions Fe^{2+} en solution est mis en évidence par ampérométrie.

PARTIE EXPERIMENTALE

Minéralisation

La minéralisation a pour objet la destruction de la matière organique et la production en solution des hétéroéléments à doser sous forme titrable. Comme il a été rappelé, elle comprend deux phases: l'attaque proprement dite du prélèvement analytique et l'oxydation éventuelle des ions porteurs de l'élément à doser en une autre forme ionique appropriée au titrage.

L'attaque proprement dite, effectuée par un mélange d'acides sulfurique et nitrique concentrés, est dérivée de celle qui a déjà été utilisée, dans notre Service, pour le dosage de l'arsenic dans les composés organiques;[5] elle est généralement applicable à la mise en solution des hétéroéléments portés par des molécules organiques. Seul varie, suivant la nature de la molécule organique et de l'hétéroélément à doser, le nombre des répétitions nécessaires de cette attaque sulfonitrique.

La variante de la méthode que nous avons mise au point comporte une évaporation par chauffage, à quasi-siccité, des acides nitrique et sulfurique dans un récipient réactionnel du type micromatras de Kjeldahl, ce qui implique, pour ce dernier, une forme et des dimensions adéquates et un dispositif d'aspiration et de chauffage progressif, à réglage fin, qui sont décrits dans le paragraphe ci-après.

Appareillage de minéralisation (Fig. 1)

Le micromatras, en verre Pyrex, dans lequel est effectuée l'attaque sulfonitrique comporte une partie sensiblement sphérique, d'une capacité d'environ 5 ml (diamètre = 25 à 26 mm) et un col de 50 mm de longueur, muni à son extrémité d'un rodage femelle normalisé (n° 0).

Le dispositif d'aspiration est une rampe tubulaire de verre Pyrex, de 40 mm de diamètre, à 6 ajutages tubulaires perpendiculaires à son axe, pourvus de 6 rodages mâles (n° 0) distants de 50–60 mm et sur lesquels peuvent être ajustés les rodages femelles des matras. La rampe est fermée à ses deux extrémités et comporte, en son centre, une tubulure d'aspiration pouvant être reliée à une trompe à eau et, à une extrémité, une tubulure de communication avec l'air ambiant pouvant être fermée par un robinet de verre à pointeau de Téflon. Sur la rampe est bobiné un cordon chauffant permettant d'élever les vapeurs d'extraction de la minéralisation à une température de l'ordre de 100°.

Le dispositif de chauffage électrique des matras est composé de six éléments chauffants constitués essentiellement par des petits fours électriques semblables aux fours mobiles de certains bancs de microanalyse utilisés pour les microdosages du carbone et de l'hydrogène[1] et dont la construction est inspirée des données de Zimmerman;[6] l'âme de chaque four est un tube de porcelaine réfractaire non vernissée, de 50 mm de diamètre intérieur, de 4 mm d'épaisseur et 50 mm de longueur, sur laquelle le fil chauffant, en nichrome, est enroulé suivant des génératrices des surfaces extérieure et intérieure du cylindre réfractaire. Le fil de nichrome a une longueur de 0,75 m et un diamètre de 0,43 mm. Le four est cimenté (ciment talc-silicate de soude) à l'intérieur d'un tube réfractaire de même longueur, de 50 mm de diamètre intérieur et de 4 mm d'épaisseur. Les éléments chauffants sont disposés verticalement et centrés sous six trous, de 50 mm de diamètre, d'une platine en amiantine horizontale. (*cf.* Fig. 1.)

Chaque élément chauffant est alimenté sous tension de 40 V par l'intermédiaire d'un rhéostat de 2,2 Ω, en série, permettant de faire varier l'intensité de chauffage de 2,7–4 A.

Les matras sont posés sur des petits carrés de toile métallique obturant les trous de la platine (*cf.* Fig. 1). La très faible inertie thermique des éléments chauffants et leur montage "en cheminée à air" permet d'obtenir un réglage fin et reproductible du chauffage des matras plus aisément qu'avec une rampe à gaz classique équipée de microbrûleurs.

Attaque sulfonitrique

Les prélèvements microanalytiques sont pesés (0,5 à 4 mg), les produits solides dans des pèse-substances classiques, les produits liquides dans des gélules* (*cf.* Ref 7) ou encore dans des sachets tubulaires de terphane[8] lorsqu'ils sont altérables à l'air, et introduits dans les matras.

* Gélules n° 5—Fabricant Parke Davis—U.S.A.

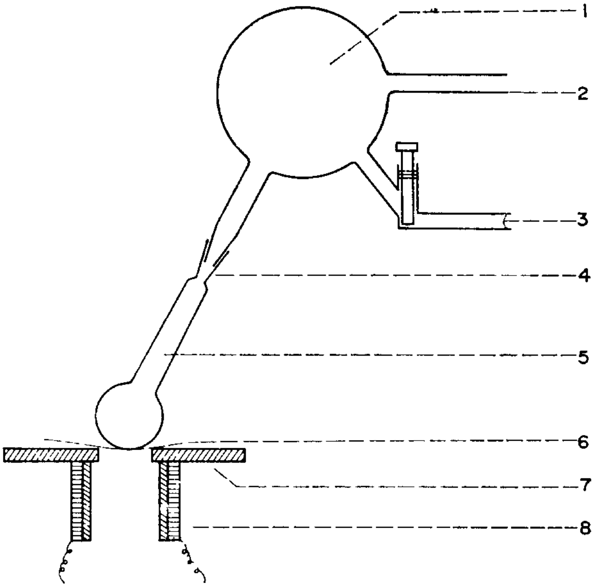


FIG. 1.—Dispositif de chauffage avec matras et rampe d'aspiration. Coupe verticale.

1 Rampe d'aspiration
2 Tubulure d'aspiration
3 Sortie tubulaire commandée par vanne en Téflon
4 Assemblage rodé
5 Matras
6 Toile métallique
7 Platine d'amiantine
8 Elément chauffant.

Sur ces prélèvements sont versées 1 ou 2 gouttes d'acide sulfurique concentré (pur pour toxicologie $d = 1{,}83$)† puis une goutte d'acide nitrique concentré (pur pour toxicologie $d = 1{,}40$).

Les matras sont posés sur les toiles métalliques des éléments chauffants et branchés par leurs rodages à la rampe d'aspiration, cette dernière étant à la pression atmosphérique, prise d'air ouverte; les éléments chauffants sont mis sous tension, les intensités étant réglées à l'aide des rhéostats à leur valeur minimale; au bout de 15 min les intensités sont réglées à leur valeur maximale de façon à chauffer les matras jusqu'à apparition des vapeurs sulfuriques.

Les éléments chauffants sont alors éteints; la prise d'air de la rampe d'aspiration est fermée et cette dernière remise sous dépression à l'aide de la trompe à eau afin de chasser des matras les vapeurs nitriques et une partie de l'acide sulfurique tandis que les composés des hétéroéléments à doser se déposent sous forme de sulfates métalliques (Mn) sur les fonds de matras ou restent en solution dans l'acide sulfurique (Cr).

Notons que nous appliquons également ce mode opératoire à la minéralisation de substances organiques contenant des hétéroéléments tels que Ni, Co, Cu, Mn, Cd, Mg, Ca, Zn, Fe et les métaux alcalins, en vue de leur dosage par complexométrie.

Oxydation des ions resultant de l'attaque sulfonitrique

Parmi les réactifs oxydants décrits dans la littérature, il importait de sélectionner pour l'usage proposé, ceux d'entre eux qui permettent d'obtenir *une vitesse d'oxydation élevée, dont simultanément l'excès peut être détruit sans nécessiter de chauffage, à cette fin, à une température trop élevée qui donnerait lieu à perte par volatilisation des composés chimiques porteurs de l'élément à doser, et dont, enfin, les produits de décomposition ne forment pas de composés volatils avec les éléments à doser et ne perturbent pas le dosage coulométrique ultérieur.*

---

† Dans le cas de substances organiques contenant du chrome il est nécessaire d'ajouter 5 gouttes supplémentaires d'acide sulfurique afin d'éviter la précipitation de sulfate chromique dont la dissolution ultérieure serait difficile.

Oxydation des ions porteurs du manganese en ions MnO_4^-

Nous avons essayé le bismuthate de sodium et le persulfate d'ammonium qui répondent aux précédentes caractéristiques.

Le premier réactif a été abandonné car son emploi implique, après réaction, une filtration[2] qui ne s'avère pas quantitative à l'échelle microanalytique du fait d'une rétention de permanganate dans le filtre. Par contre, le persulfate d'ammonium, en présence d'ions Ag^+, sous forme de nitrate[2,3] offre l'avantage d'être détruit par simple élévation de température à 80° avec dégagement d'oxygène. Cependant cette destruction s'accompagne de la formation de persels instables, mais électroactifs en solution, dont la nature n'a pu être déterminée et qui perturbent le dosage coulométrique en entachant les résultats analytiques d'une erreur soit positive soit négative correspondant à une quantité de manganèse de l'ordre de grandeur de 20 à 30 μg.

L'expérience nous a montré que la présence de quelques grains de magnésie ou d'alumine* en solution, lors de l'oxydation, permet de catalyser la destruction de ces persels.

Les produits de l'attaque sulfonitrique sont repris, dans chaque matras, par de l'eau distillée; la solution obtenue est ensuite transvasée dans un bécher de 100 ml, de forme haute, où les eaux de lavage quantitatif du matras, à l'eau distillée, sont également collectées. A la solution ainsi obtenue dont le volume doit être d'environ 10 ml sont ajoutés 200 à 300 mg de persulfate d'ammonium, une dizaine de milligrammes de nitrate d'argent et une pointe de microspatule de magnésie ou d'alumine granulée.

Le bécher est recouvert d'un verre de montre et la solution est portée puis maintenue à l'ébullition jusqu'à cessation complète du dégagement gazeux provoqué par la destruction du persulfate d'ammonium, ce qui requiert un temps de 20 à 30 min. La solution est alors refroidie sous un courant d'eau et transvasée quantitativement, dans le vase de titrage coulométrique (son volume total, dont les eaux de lavage du bécher, doit être de l'ordre de grandeur de 40 ml).

Oxydation des ions porteurs du chrome en ions $Cr_2O_7^{2-}$

Nous avons préféré l'acide perchlorique[4] au persulfate d'ammonium en présence d'argent pour effectuer cette oxydation, du fait de sa réaction sélective; il permet en effet d'oxyder les ions porteurs du chrome en ions $Cr_2O_7^{2-}$ sans oxyder les ions porteurs du manganèse en ions MnO_4^- et par conséquent de doser éventuellement le chrome en présence de manganèse.

En outre, l'action de l'acide perchlorique est rapide et ne nécessite pas, comme dans le cas du persulfate d'ammonium, la destruction de l'excès de réactif en vue du titrage coulométrique ultérieur.

Toutefois la présence d'ions Cl^- dans l'acide perchlorique du commerce donne lieu à la formation de chlorure de chromyle volatil avec perte de chrome; afin d'éviter cet inconvénient il suffit d'éliminer les ions Cl^- en les précipitant sous forme de chlorure d'argent par des ions Ag^+ (nitrate d'argent).

Aux produits de l'attaque sulfonitrique sont ajoutés, dans le matras, 1 ml d'acide perchlorique R. P. puis quelques cristaux de nitrate d'argent (environ 10 mg).

Le matras est alors chauffé, sur la veilleuse d'un bec Bunsen, avec précaution, afin de ne pas atteindre la température de décomposition de l'acide perchlorique se décelant par un fort dégagement gazeux, pendant 1–2 min, temps nécessaire pour l'oxydation du chrome sous forme d'ions bichromiques.

Il convient de remarquer qu'une prolongation du chauffage pendant 5 min ne donne par lieu à perte de chrome.

La solution obtenue dans le matras est alors transvasée directement, ainsi que les eaux de lavages, dans le récipient de titrage coulométrique. Le volume total de la solution doit être de l'ordre de grandeur de 40 ml.

Titrage coulométrique

Les principes des titrages coulométriques et les appareils permettant leur application ont été décrits par maints auteurs[5–12] qui mettent en oeuvre des sources variées de courant, avec régulation d'intensité et des méthodes et systèmes divers de détection de fin de titrage.

Il est aisé, par l'étude des courbes voltampéromètriques, en solution[10,11] de mettre en évidence les conditions électrochimiques dont la réalisation est requise en vue de la génération quantitative en solution, par simple électrolyse, d'un oxydant ou d'un réducteur.

Par contre, le choix de la méthode indicatrice de fin de titrage est plus délicat. En effet, la reproductibilité des résultats des dosages et la sensibilité globale de la méthode dépendent, en grande partie, de la reproductibilité et de la sensibilité de la réponse des électrodes utilisées pour la détection des espèces électroactives, en solution. La détection par ampérométrie entre électrodes bimétalliques (*cf.* Ref. 10) est à la fois fidèle et sensible sous réserve que la surface des électrodes en contact avec la solution soit inaltérable et de dimensions appropriées à la sensibilité requise, ce qui est compatible avec nos conditions opératoires; nous avons donc adopté cette méthode.

* Magnésie frittée en grains de 1 mm—Fournisseur Desmarquet—France. Alumine "ALCEL" en grains de 1 mm—Fournisseur Desmarquet—France.

Il convient cependant de remarquer qu'elle ne permet pas de déterminer le point final proprement dit d'un titrage; elle permet seulement d'arrêter ce dernier lorsqu'un paramètre de titrage, en l'occurence la concentration des ions ou du réactif titrants engendrés in situ par électrolyse, atteint une valeur déterminée et précise. Dans le présent travail il s'agit de la concentration des ions Fe^{2+}.

L'application de la méthode implique donc que soient déterminées, avant les titrages, les quantités d'électricité qui ont servi à la génération, dans les solutions à titrer, des excès d'ions Fe^{2+} correspondant aux concentrations de ces réactifs définissant les points d'arrêt de titrage. Elles doivent en effet être soustraites des quantités totales d'électricité consommées au cours des titrages coulométriques pour calculer les quantités d'électricité équivalentes aux espèces chimiques à titrer.

Ainsi, compte tenu des conditions électrochimiques à réaliser pour l'électrolyse et de celles qui sont inhérentes à la mesure finale ampérométrique, la reproductibilité des résultats des titrages dépend essentiellement des facteurs suivants:

—volume de la solution,

—concentration des acides et des sels en solution,

—agitation de la solution.

Il vient s'y ajouter la constance du courant d'électrolyse imposée par la méthode de mesure coulométrique mise en oeuvre qui est ramenée à une mesure de temps (*cf.* ci-après).

Appareillage de titrage coulométrique

L'appareillage que nous employons est semblable à celui qui a été déjà mis en oeuvre par d'autres auteurs.[11] Il comprend le coulomètre proprement dit, un détecteur de fin de titrage et une cellule électrochimique.

Coulométre. Cet instrument est un Chronoamperostat Tacussel, type CEAM D 3 qui réunit, en un seul appareil un ampèrostat et un chronomètre électronique. L'ampèrostat permet de régler (de 10^{-5} à 10^{-1} A), de choisir et de maintenir constante l'intensité i du courant d'électrolyse; le chronomètre permet de mesurer avec précision (à 0,01 sec près) le temps t de passage du courant d'intensité imposée i et par conséquent, de connaître, à chaque instant, la quantité d'électricité ($q = it$) consommée par l'électrolyse.

Détecteur de fin de titrage. Cet appareil est une Unité de détection ampérométrique Tacussel, type ALO4, qui permet d'établir une tension imposée (réglable de 0 à 1000 mV). Il comporte un ampèremètre à cadre mobile qui mesure l'intensité du courant qui passe entre les électrodes indicatrices et qui est pourvu d'un index à position réglable dans toute l'étendue de l'échelle de mesure (cadran). Le franchissement de l'index par l'aiguille de l'ampèremètre donne lieu à coupure du courant d'électrolyse par l'intermédiaire d'un relais.

Cellule èlectrochimique—(Fig. 2). La cellule électrochimique comprend essentiellement un récipient, deux électrodes d'électrolyse et deux électrodes indicatrices. Le récipient est un cylindre en verre Pyrex, à fond plat, à section carrée, d'une capacité de 50 ml dont l'orifice comporte un rodage plan sur lequel se pose un couvercle de même forme d'environ 35 mm de hauteur. Le fond du couvercle est pourvu de quatre ajutages à rodages coniques femelles qui permettent le passage de quatre électrodes et d'un courant d'un gaz inerte; il est en outre percé d'un trou de 3 mm de diamètre qui permet éventuellement l'injection d'un réactif dans la solution à titrer. Cet ensemble permet d'effectuer des réactions électrochimiques en solution en l'absence d'oxygène.

Les électrodes d'électrolyse comportent une électrode génératrice employée comme cathode (réduction des ions MnO_4^- et $Cr_2O_7^{2-}$) et une électrode auxiliaire. La premiére est constituée par une plaque de platine d'une superficie de 200 mm^2 (20 × 10 mm) soudée à un fil de platine de 0,1 mm de diamètre[4] qui plonge dans la solution à titrer; la seconde est un simple fil de platine de 1 mm de diamètre qui plonge dans une solution de l'électrolyte support utilisé au sein d'un compartiment (tube de verre Pyrex de 12 mm de diamètre porteur d'un rodage mâle s'adaptant sur un rodage femelle du couvercle de la cellule) isolé de la solution à titrer par une plaque de verre Pyrex fritté n° 4. Les deux fils de platine servent à connecter ces électrodes à l'ampérostat.

Les électrodes indicatrices sont deux fils de platine de 0,5 mm de diamètre isolés à leurs parties supérieures par des gaines de verre qui leur sont collées par chauffage. Leurs parties inférieures plongent dans la solution à titrer; l'une a la forme d'une hélice à quatre spires de 5 mm de diamètre (longueur de fil: 60 mm) tandis que l'autre, rectiligne, coïncide avec l'axe de cette hélice (longueur de fil: 10 mm). Les deux fils de platine (parties supérieures) servent à connecter les électrodes au détecteur de fin de titrage.

Titrage coulométrique des ions MnO_4^- et $Cr_2O_7^{2-}$

Les dosages des ions permanganiques et bichromiques sont basés sur le même principe. Les modes opératoires correspondants ne diffèrent que par l'intensité du courant d'électrolyse qui permet la réduction des ions Fe^{3+} en ions Fe^{2+}; elle est fixée a 10 mA dans le cas du manganèse et à 3 mA dans le cas du chrome afin que les durées d'électrolyse ne soient pas trop élevées et restent du même ordre de grandeur malgré les nombres différents d'électrons échangés par le manganèse et le chrome dans les réactions de réduction.

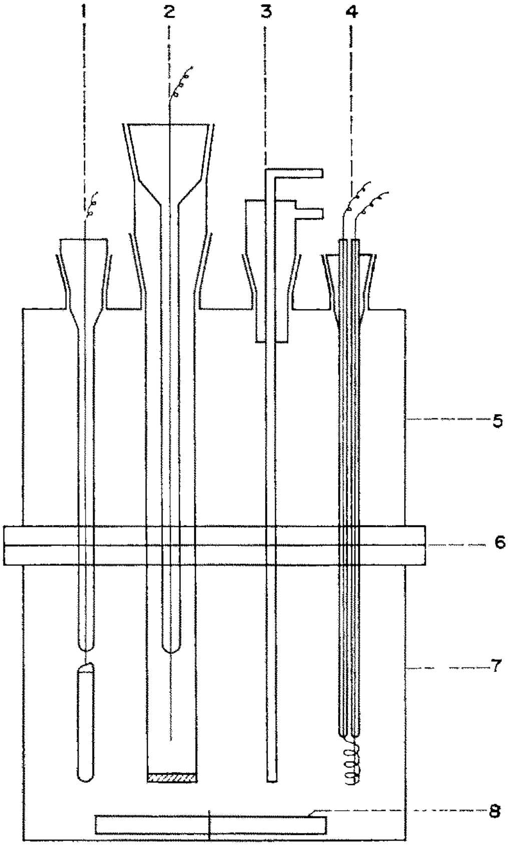


FIG. 2.—Cellule de titrage coulométrique.

1 Electrode génératrice de coulométrie
2 Electrode auxiliaire de coulométrie avec compartiment séparé
3 Système de barbotage d'azote
4 Electrodes indicatrices
5 Couvercle de la cellule avec rodages normalisés
6 Rodage plan
7 Vase de titrage
8 Barreau d'agitation.

Determination du point final de titrage—mesure du "seuil"

L'excès d'ions Fe^{2+} qui apparaît en solution dès que tous les ions MnO_4^- et $Cr_2O_7^{2-}$ sont réduits, doit permettre de mettre en évidence le point final de titrage; afin que le titrage soit précis, il importe que la concentration des ions Fe^{2+} atteinte soit aussi faible que possible et corresponde à une quantité de manganèse ou de chrome ne dépassant pas 3–5 μg.

Par ailleurs, avec l'appareillage utilisé, l'ordre de grandeur du minimum de l'intensité du courant susceptible d'être décelé entre les deux électrodes indicatrices est de 2–3 μA.

En vue d'assurer une sensibilité suffisante du titrage coulométrique, l'étude des courbes intensités-potentiels, dans des solutions de compositions identiques à celles de nos solutions à titrer, montre qu'il est alors nécessaire d'imposer une tension de 600 mV entre les électrodes indicatrices.

Dans la pratique l'intensité du courant indicatrice du point final de titrage est fixée à 3 μA*;

---

* Dans le cas particulier du dosage de quantités de chrome correspondant à des concentrations inférieures à $10^{-5}N$, la réaction de réduction des ions $Cr_2O_7^{2-}$ par les ions Fe^{2+} n'est plus quantitative de sorte que la concentration en ions Fe^{2+} correspondant au "seuil" est atteinte avant le "point d'équivalence", ce qui conduit à l'obtention de résultats erronés par défaut. Pour pallier cet inconvénient, l'intensité de courant indicatrice de fin de titrage est alors fixée à un ordre de grandeur de 10–15 μA.

la quantité d'électricité qui est alors nécessaire lors de la simple réduction électrolytique des ions Fe^{3+} pour atteindre la concentration en ions Fe^{2+} correspondant au courant de 3 μA déclenchant l'arrêt de l'électrolyse est dénommée seuil coulométrique ou "seuil". Elle peut être exprimée en coulombs, ou plus simplement, à un coefficient près, l'intensité du courant d'électrolyse étant fixée et constante, en unités de temps (secondes).

Elle devra être retranchée de la quantité totale d'électricité consommée par la réduction quantitative des ions MnO_4^- ou $Cr_2O_7^{2-}$.

Le "seuil" est mesuré dans une solution aqueuse d'ions ferriques acidifiée et additionnée de nitrate d'argent oú plongent les électrodes. Celles-ci sont décapées par quelques gouttes d'acide nitrique ajoutées à la solution avant leur immersion. La solution est dégazée par barbotage d'un courant d'azote. Ce dégazage a pour double effet de chasser de la solution les gaz oxydants dissous, c'est à dire l'oxygène ainsi que, dans le cas du dosage du chrome, le chlore provenant de l'acide perchlorique utilisé pour l'oxydation des produits de l'attaque sulfonitriques. L'absence d'oxygène permet d'abaisser le courant résiduel à 0,5 μA* et corrélativement de déterminer la valeur du "seuil" avec une plus grande reproductibilité.

Le système des quatre électrodes est plongé dans une solution aqueuse dont le volume total est ajusté à 40 ml (à 5 ml près) et contenant 10 ml d'une solution d'acide sulfurique 4*N*, environ 10 mg de nitrate d'argent, 0,2 g de sulfate ferrique PA et 2 à 3 gouttes d'acide nitrique concentré (pour toxicologie: $d = 1,40$).

Le courant d'azote† est alors envoyé dans la solution pendant toute la durée de la détermination. Après 5 min de barbotage, l'électrolyse qui donne lieu à la réduction des ions Fe^{3+} est déclenchée et se poursuit jusqu'à son arrêt automatique. Le "seuil" est alors mesuré par le temps t_s indiqué par le coulomètre; il est de l'ordre de grandeur de 4 à 6 sec et doit être reproductible à 1 sec près; il est évidemment supérieur à cette valeur et atteint 20 à 30 sec dans le cas particulier ou l'intensité de courant indicatrice est fixée à 10–15 μA.

Titrage proprement dit

Le mode opératoire est semblable à celui qui vient d'être décrit pour la mesure du "seuil". A la solution obtenue par minéralisation du prélèvement analytique recueillie dans le vase de titrage coulométrique et dont le volume est préalablement ajusté à 40 ml à l'aide d'eau distillée, sont ajoutés 0,2 g de sulfate ferrique et 2 à 3 gouttes d'acide nitrique; le système d'électrodes est mis en place et la solution dégazée; l'électrolyse est alors déclenchée; lors de son arrêt automatique, le temps t_x mesuré par le coulomètre correspond à la quantité d'électricité consommée pour la réduction quantitative des ions MnO_4^- ou $Cr_2O_7^{2-}$.

Calcul des résultats. L'application de la loi de Faraday conduit aux formules de calcul suivantes:

$$\text{Mn}\ \% = \frac{113{,}86(t_x - t_s)}{m}$$

$$\text{Cr}\ \% = \frac{53{,}89\,(t_x - t_s)}{m}$$

dans lesquelles *m* est la masse du prélèvement analytique exprimée en microgrammes.

Elles ont été établies pour une intensité de courant d'électrolyse égale à 10 mA dans le cas du manganèse, à 3 mA dans le cas du chrome et les valeurs numériques suivantes des constantes: Faraday = 96480 C; Mn = 54,94; Cr = 52,00.

RESULTATS ET CONCLUSION

Il apparaît que les méthodes décrites pour les dosages du manganèse et du chrome, qui comportent une attaque sulfonitrique suivie d'une oxydation des ions formés et un titrage par électrolyse coulométrique à intensité constante, fournissent des résultats (Tableaux I et II) dont la précision est comparable à celle des méthodes classiques de la microanalyse organique élémentaire, caractérisée par l'ordre de grandeur des erreurs absolues.

Il est cependant certains cas extrêmes tels que celui du dosage du chrome dans le nitrure de chrome (dont la teneur élevée en élément à doser (78,79%) qui imposent d'effectuer des prélèvements analytiques décimilligrammiques, en vue de l'obtention

---

* Le courant résiduel est défini par le courant apparaissant entre les deux électrodes indicatrices plongées dans la solution en présence de toutes les espèces électroactives nécessaires au titrage, à l'exception de l'espèce oxydante ou réductrice produite électrochimiquement.

† Azote: qualité R de la Société "L'Air liquide".

TABLEAU I.—MANGANESE

Substance	Mn % calculé	m, mg	Masses de manganése		Mn % trouvé	Ecart Mn % tr.-Mn % calc.
			calculée μg	trouvée μg		
Permanganate de potassium	34,76	2,415	839	841	34,8	0,0
		1,375	478	478	34,8	0,0
		4,147	1441	1438	34,7	−0,1
Sulfate de manganèse $MnSO_4, 6H_2O$	32,50	0,814	265	266	32,7	+0,2
		2,360	767	764	32,4	−0,1
		1,373	446	444	32,3	−0,2
		1,959	637	638	32,6	+0,1
		0,997	324	322	32,3	−0,2
Produits organométalliques de recherche	16,25	2,280	371	370	16,2	0,0
		3,033	493	492	16,2	0,0
		4,275	695	688	16,1	−0,2
		4,005	651	655	16,4	+0,1
	16,74	1,287	215	215	16,7	0,0
		4,380	733	730	16,7	−0,1
		2,100	352	351	16,7	0,0
		2,143	359	364	17,0	+0,3
		1,695	284	285	16,8	+0,1

TABLEAU II.—CHROME

Substance	Cr % calculé	m, mg	Masses de chrome		Cr % trouvé	Ecart Cr % tr.-Cr % calc
			calculée μg	trouvée μg		
Tris (phénylbutanedione 1,3) chrome*	9,71*	2,245	218	216	$9{,}6_2$	−0,1
		2,976	289	291	$9{,}7_8$	+0,1
		0,918	89	87	9,4	−0,3
		2,710	263	267	$9{,}8_4$	+0,1
		3,070	298	298	$9{,}7_1$	0
Produits organométalliques de recherche	16,60	2,176	361	363	$6{,}6_7$	+0,1
		5,221	867	868	$16{,}6_2$	0,0
		2,222	369	370	$16{,}6_3$	0,0
	17,20	2,749	473	471	$17{,}1_4$	−0,1
	20,14	3,790	763	774	$20{,}4_3$	+0,3
		3,590	723	729	$20{,}3_1$	+0,2
		2,866	577	575	$20{,}0_6$	−0,1
	16,44	2,206	363	364	$16{,}4_8$	0,0
	14,97	2,670	400	402	$15{,}0_4$	+0,1
		3,731	559	556	$14{,}9_0$	−0,1
Nitrure de chrome (N Cr)	78,79	0,1930	152	153	79,2	+0,5
		0,1872	147	148	79,2	+0,4
		0,2823	222	223	79,0	+0,2
		0,4861	383	380	78,2	−0,6
		0,4390	346	343	78,2	−0,6

de minéralisations quantitatives), où l'ordre de grandeur de l'erreur absolue peut dépasser celui de l'erreur classique; cependant l'ordre de grandeur de l'erreur relative reste alors satisfaisant.

Dans les conditions définies dans cette étude, toutes quantités de métaux peuvent être dosées sous réserve de rester inférieures à 800 μg, masse qui définit, dans ce cas, la limite supérieure du domaine microanalytique; en ce qui concerne la limite inférieure elle peut être abaissée à un ordre de grandeur de 40–30 μg, sous réserve de définir un "seuil" de fin de titrage correspondant à une intensité de courant indicatrice voisine de 15 μA.

Par ailleurs certaines substances, figurant sur les tableaux de résultats et marqués d'un astérisque, ne sont pas analytiquement pures; elles ont été fournies par le "National Bureau of Standards" de Washington avec une teneur certifiée de l'élément à doser; cette dernière, également marquée d'un astérisque est reportée dans les tableaux au lieu de la teneur calculée; les écarts reportés sont, dans ce cas, les différences entre les teneurs trouvées et les teneurs certifiées.

Summary—Constant-current coulometric titration is applied to the determination of manganese and chromium contained in organic compounds. These compounds are decomposed in a mixture of sulphuric and nitric acids. The Mn and Cr are oxidized by ammonium persulphate to MnO_4^- and by perchloric acid to $Cr_2O_7^{2-}$ respectively. MnO_4^- and $Cr_2O_7^{2-}$ are titrated by Fe^{2+} electrolytically generated from Fe^{3+} by constant-current eletrolysis, with amperometric end-point detection,

Zusammenfassung—Mangan und Chrom in organischen Verbindungen werden mit Hilfe einer coulometrischen Titration bei konstantem Strom bestimmt. Die Verbindungen werden in einem Gemisch aus Schwefel- und Salpetersäure aufgeschlossen. Mn wird mit Ammoniumpersulfat zu MnO_4^- und Cr mit Überchlorsäure zu $Cr_2O_7^{2-}$ oxidiert. MnO_4^- und $Cr_2O_7^{2-}$ werden mit Fe^{2+} titriert, das elektrolytisch aus Fe^{3+} durch Elektrolyse bei konstantem Strom erzeugt wird. Der Endpunkt wird amperometrisch ermittelt.

BIBLIOGRAPHIE

1. R. Lévy, *Monographies de chimie organique*, Vol. IV, *Microanalyse organique élémentaire qualitative et quantitative*, Masson, Paris, 1961.
2. A. Libertti et L. Ciavatti, *Mettalurgia Italiana*, 1958, 50.
3. J. S. Hetman, *Analyst*, 1956, 81, 543.
4. S. Lynn et D. M. Mason, *Anal. Chem.*, 1952, **24**, 1855.
5. R. Lévy, *Bull. Soc. Chim. France*, 1956, 517.
6. W. Zimmermann, *Mikrochem. Mikrochim. Acta*, 1943, **31**, 149.
7. E. Debal, *Mikrochim. Acta*, 1964, 272.
8. R. Reverchon, Communication Verbale—Journées de Microanalyse organique organisées par la Société Chimique de France et la Société de Chimie Industrielle les 18–19 mars 1971.
9. G. Charlot, *Les Méthodes de la Chimie Analytique*, Masson, Paris, 1956.
10. B. Lambling et B. Trémillon, *Les Méthodes èlectrochimiques*, Masson, Paris, 1959.
11. R. Gauguin, *Chim. Anal*, 1954, **36**, 92.
12. L. Meites, *Anal. Chem.*, 1952, **24**, 1057.

Talanta, 1972, Vol. 19, pp. 157 to 161. Pergamon Press. Printed in Northern Ireland

APPLICATIONS DE L'IODOMETRIE COULOMETRIQUE AUX DOSAGES MICROANALYTIQUES DE L'ARSENIC, DE L'ANTIMOINE ET DU CUIVRE DANS LES COMPOSES ORGANIQUES

M. BIGOIS
(avec la collaboration technique de M. MARCHAND)
Service Central de Microanalyse du Centre National de la Recherche
Scientifique, 2, rue Henry Dunant, 94—Thiais, France

(*Reçu le* 12 *juillet* 1971. *Accepté le* 23 *août* 1971)

Résumé—Une méthode de microdosage de l'arsenic, de l'antimoine et du cuivre dans les composés organométalliques est décrite. Les substances sont décomposées dans un mélange d'acides sulfurique et nitrique. Les produits de décomposition sont alors oxydés par l'eau oxygénée dans le cas de l'arsenic et par le permanganate de potassium dans le cas de l'antimoine afin d'obtenir respectivement les ions AsO_4^{3-} et SbO_4^{3-}. Dans le cas du cuivre, les ions Cu^{2+} sont obtenus directement comme produit de décomposition. L'iode engendré par l'électrolyse d'une solution aqueuse d'iodure de potassium est l'agent titrant, avec une solution de thiosulfate de sodium comme agent intermédiaire (fin de titrage ampérométrique). L'iode produit est mesuré coulométriquement.

LE CARACTÈRE réducteur des ions iodures en solution aqueuse peut être mis à profit pour le dosage de l'arsenic, de l'antimoine et du cuivre dans les composés minéraux comme l'ont montré de nombreux auteurs (*cf.* citation 1). Par ailleurs nous avons déjà mis en évidence l'intérêt de l'application des méthodes coulométriques au dosage microanalytique de certains métaux (Mn, Cr) dans les composés organiques.[2] En ce qui concerne le dosage microanalytique de l'arsenic, de l'antimoine et du cuivre dans les composés organiques, il est également possible d'appliquer les méthodes coulométriques sous forme de l'iodométrie coulométrique. Il convient alors de minéraliser les composés organiques porteurs de ces hétéroéléments en vue de l'obtention d'espèces ioniques représentatives de ces derniers et susceptibles d'être réduites par les ions I^-.

La mise en oeuvre, à cette fin, de réactions d'oxydoréduction appropriées permet, en outre, d'effectuer avec spécificité le titrage de ces éléments en présence de métaux susceptibles de se trouver simultanément présents dans les produits soumis à l'analyse.

Une attaque sulfonitrique fournit des mélanges d'ions porteurs d'arsenic et d'antimoine tri et pentavalents qui doivent être oxydés en ions arséniques AsO_4^{3-} et antimoniques SbO_4^{3-} en vue de leurs titrages. Les réactifs oxydants correspondants utilisés sont respectivement l'eau oxygénée, dans le premier cas[3] et le permanganate de potassium, dans le second.[4]

Les ions AsO_4^{3-} et SbO_4^{3-} sont réduits par des ions I^- (iodure de potassium) en milieu acide, avec formation d'iode libre; l'iode est à son tour réduit par un excès d'une solution titrée de thiosulfate de sodium et cet excès dosé par de l'iode engendré par électrolyse des ions I^- en solution; le point final de titrage qui correspond à l'apparition d'un excès d'iode libre, en solution est mis en évidence par ampérométrie. Le titre du thiosulfate employé est déterminé par l'iode électrolytique de façon identique. L'attaque sulfonitrique fournit directement les ions cuivriques Cu^{2+} qui sont titrés suivant le même principe que les ions AsO_4^{3-} et SbO_4^{3-}.

PARTIE EXPERIMENTALE

Minéralisation

L'appareillage de minéralisation est identique à celui que nous avons antérieurement decrit.[2]

Attaque sulfonitrique. Le mode opératoire d'attaque sulfonitrique des composés organiques précédemment décrit[2] (qui permet notamment de doser les métaux qu'ils contiennent par complexométrie) est directement applicable dans le cas du dosage du cuivre par iodométrie coulométrique.

Dans les cas de l'arsenic et de l'antimoine il est nécessaire d'employer des quantités supérieures d'acide sulfurique, soit 5 à 10 gouttes, afin d'éviter, surtout dans le cas de l'arsenic, la précipitation d'oxydes d'arsenic sublimables à température élevée.

Il importe en outre de noter que l'obtention de solutions parfaitement limpides contenant quantitativement l'arsenic et l'antimoine à doser peut nécessiter, parfois, trois attaques successives suivant le mode opératoire déjà cité.[2]

Oxydation des ions porteurs de l'arsenic en ions AsO_4^{3-}. Aux produits de l'attaque sulfonitrique, deux gouttes d'eau oxygénée (à 100 volumes) sont ajoutées, dans le matras. Ce dernier est alors replacé sur la rampe de minéralisation et chauffé lentement à la pression atmosphérique, jusqu'à cessation du bouillonnement dû à la décomposition de l'eau oxygénée. Les dernières traces de ce réactif doivent être détruites; à cette fin, il est nécessaire d'élever la température jusqua'à ébullition de l'acide sulfurique; cette dernière ne doit durer que quelques secondes afin d'éviter des pertes d'arsenic par volatilisation sous forme d'hémipentoxyde.

La solution obtenue dans le matras est alors transvasée dans le vase de titrage coulométrique ainsi que les eaux de lavage. Le volume total de liquide doit y être de l'ordre de grandeur de 40 ml.

Oxydation des ions porteurs de l'antimoine en ions SbO_4^{3-}. La faible quantité d'acide sulfurique utilisée lors de l'attaque sulfonitrique conduit à une précipitation d'une partie de l'antimoine sous forme d'oxydes. Les essais d'oxydation par l'eau oxygénée[5] visant simultanément la mise en solution se sont avérés infructueux; nous avons attribué cet échec au défaut de réaction de l'eau oxygénée sur le précipité antimonié. Par contre, nous avons pu effectuer quantitativement cette oxydation et la mise en solution grâce à l'emploi du permanganate de potassium.

Aux produits de l'attaque sulfonitrique sont ajoutés, dans le matras, une dizaine de gouttes d'eau distillée et 20 à 30 mg de permanganate de potassium cristallisé.

Le matras est alors replacé sur la rampe de minéralisation et chauffé lentement à la pression atmosphérique jusqu'à la température d'ébullition de l'acide sulfurique. Afin d'éliminer l'excès d'ions permanganiques et de solubiliser l'hémipentoxyde d'antimoine obtenu, 7 à 8 gouttes d'acide chlorhydrique (pur pour analyse) et quelques gouttes d'eau distillée sont ajoutées dans le matras. En vue de chasser le chlore formé par réaction de l'acide chlorhydrique sur le permanganate, le matras est à nouveau chauffé sur la rampe, à basse température, afin d'éviter les pertes d'antimoine par volatilisation du pentachlorure d'antimoine.

La solution obtenue dans le matras est alors transvasée ainsi que les eaux de lavage dans le récipient de titrage coulométrique. Le volume total du liquide doit y être de l'ordre de grandeur de 40 ml.

Titrage coulométrique

L'appareillage permettant le titrage coulométrique est identique à celui qui a été antérieurement décrit.[2] Le système oxydoréducteur qui permet de mettre en évidence la fin de titrage est, ici, le couple iode–iodure; il s'agit donc, dans ce cas, de détecter un excès d'iode dont la concentration est contrôlée par ampérométrie par l'apparition d'un courant passant entre deux électrodes de platine polarisées sous 150 mV.

Titrages coulométriques des ions AsO_4^{3-}, SbO_4^{3-} *et* Cu^{2+}. Les titrages des ions arséniques, antimoniques et cuivriques se ramènent tous à une iodométrique coulométrique. L'intensité du courant de l'électrolyse qui donne lieu à génération d'iode par oxydation des ions I^- est fixée à 3 mA. Les titrages des ions AsO_4^{3-} et SbO_4^{3-} sont effectués en milieu acidifié par l'acide chlorhydrique afin de faciliter la réaction ultérieure d'oxydoréduction. Le titrage des ions Cu^{2+} qui donne lieu à la précipitation d'iodure cuivreux est effectué en milieu acidifié par l'acide acétique et l'acide nitrique en présence de gélatine, comme d'aucuns[6] l'ont préconisé pour le dosage des ions Cl^- par argentométrie.

Par ailleurs, l'oxygène dissous dans les solutions à titrer est susceptible de fausser les dosages iodométriques du fait de l'oxydation facile des ions I^- en milieu acide. Afin d'éviter cette cause d'erreur les solutions sont désoxygénées avant l'addition d'iodure du potassium par barbotage d'un courant d'azote pendant un temps suffisant. L'expérience montre que ce dégazage permet d'abaisser suffisamment la concentration de l'oxygène dissous pour éliminer toute perturbation du titrage iodométrique.

Determination du point final de titrage—mesure du seuil

Le titrage électrochimique consiste à mesurer, à l'aide d'iode engendré par électrolyse coulométrique d'iodure de potassium (oxydation anodique des ions I^-), l'excès de thiosulfate introduit dans la solution à titrer après la libération d'iode par oxydation antérieure des ions I^- (iodure de potassium) par les ions AsO_4^{3-}, SbO_4^{3-} ou Cu^{2+}. L'excès d'iode libéré qui apparaît en solution dès que tous les ions $S_2O_3^{2-}$ sont réduits doit permettre de mettre en évidence le point final du titrage de l'excès de thiosulfate.

En vue d'assurer une sensibilité suffisante du titrage coulométrique, l'étude des courbes intensités-potentiels montre qu'avec l'appareil de détection utilisé[2] il est nécessaire, dans le cas du système iode-iodure et dans les conditions du titrage, d'imposer une tension de 150 mV entre les électrodes indicatrices.

Dans la pratique, l'intensité de courant indicatrice du point final de titrage est fixée à 3 à 4 μA; la quantité d'électricité qui est alors nécessaire, lors de la simple oxydation électrolytique d'ions I^-, pour atteindre la concentration en iode libre correspondant au courant de 3-4 μA déclenchant l'arrêt de l'électrolyse est le "seuil". Elle est exprimée en unités de temps puisque l'intensité du courant d'électrolyse est fixée et constante; son ordre de grandeur correspond à 5 à 6 μg d'arsenic et 9 à 10 μg d'antimoine ou de cuivre. Elle est retranchée de la quantité d'électricité consommée par l'oxydation quantitative de l'excès d'ions $S_2O_3^{2-}$.

Le système des quatre électrodes est plongé dans une solution dont le volume total est ajusté à 40 ml (à 3 à 4 ml près). Dans le cas des dosages de l'arsenic et de l'antimoine cette solution aqueuse contient un mélange de 10 ml d'une solution d'acide chlorohydrique 4N et de 10 ml d'une solution d'acide sulfurique 4N; dans le cas du dosage du cuivre elle est constituée par un mélange d'acide acétique (pur P. A.) et d'acide nitrique (pur pour toxicologie; $d = 1{,}4$),[6] dans un rapport volumique de 10/1, auquel sont ajoutés 5 g de gélatine par litre de solution.* Le courant d'azote est alors envoyé dans la solution où il barbote pendant 5 min; il est ensuite maintenu au dessus de la solution à titrer à laquelle est ajouté 1 g d'iodure de potassium. L'électrolyse qui donne lieu a l'oxydation des ions I^- est déclenchée et se poursuit jusqu'à son arrêt automatique. Le "seuil" est alors mesuré par le temps t_S indiqué par le coulomètre; il est de l'ordre de grandeur de 4 à 5 sec et doit être reproductible à moins d'une seconde près.

Determination du titre de la solution de thiosulfate de sodium

Suivant la pratique classique, les solutions de thiosulfate de sodium sont préparées un mois avant leur emploi à la concentration 10^{-1} N, et stabilisées par addition de carbonate de sodium.[5] Elles sont diluées à la concentration 10^{-2} N au moment de leur emploi par volumes de 1 litre.

Avant tous les dosages il est nécessaire de déterminer, par coulométrie, le titre exact de la solution de thiosulfate ainsi préparée. A cette fin, dans une solution venant de servir à la détermination du "seuil" et contenant donc la quantité d'iode correspondant au point final de titrage, il est ajouté 1 ml de la solution de thiosulfate à titrer, le courant d'azote étant maintenu au dessus de la solution. L'électrolyse se déclenche alors automatiquement.

Le temps t_N d'électrolyse sous intensité de courant de 3 mA, mesuré lors de l'arrêt automatique de celle-ci, correspond à la quantité d'électricité nécessaire à l'oxydation par l'iode électrolytique de la quantité de thiosulfate introduite; il est la mesure du titre électrochimique du thiosulfate. Si le titre du thiosulfate était exactement 10^{-2} N, ce temps devrait être égal à 321,6 sec; le temps réel doit être l'objet de 3 ou 4 déterminations et l'écart maximal des valeurs obtenues ne doit pas dépasser 1 seconde; le temps moyen est adopté comme titre électrochimique du thiosulfate.

Titrage proprement dit

La mode opératoire est semblable à celui qui vient d'être décrit pour la mesure du "seuil" et du titre du thiosulfate. Les solutions d'ions AsO_4^{3-} ou SbO_4^{3-} ont été transvasées dans le récipient de titrage coulométrique après le traitement oxydant (voir minéralisation). Dans le cas du dosage du cuivre la solution d'attaque sulfonitrique a été directement transvasée dans ce récipient ainsi que les eaux de lavage (à l'eau distillée) du matras.

Le volume de chacune de ces solutions a été ajusté à 40 ml (à 3 à 4 ml près) dans le récipient de titrage. La solution est alors dégazée par barbotage d'azote, pendant 5 min comme précédemment et 1 g d'iodure de potassium cristallisé lui est alors ajouté tandis que le courant d'azote est maintenu au dessus de la solution.

L'iode libéré est ensuite réduit par addition de la solution de thiosulfate de sodium précédemment titrée. Cette opération est effectuée manuellement ou automatiquement grâce à l'emploi d'une électroburette Tacussel commandée par le détecteur ampèrométrique de fin de titrage; l'introduction

---

* L'addition de sulfocyanure de potassium[7] (concentration de 10^{-2} M) à l'électrolyte permet de doser des quantités de cuivre de l'ordre de grandeur de 50 μg, grâce au faible produit de solubilité du sulfocyanure cuivreux qui est inférieur à celui de l'iodure cuivreux.

† Azote de qualité "R" fourni par la Société "L'Air liquide".

de la solution de thiosulfate est arrêtée dès que la concentration de l'iode en solution devient inférieure à celle qui correspond au "point final de titrage".

Après 10 min d'attente, temps nécessaire à la réaction des ions I^- sur les ions réductibles, l'électrolyse est déclenchée et s'arrête automatiquement au bout d'un temps t_x.

Calcul des résultats. L'application de la loi de Faraday conduit aux formules de calcul suivantes:

$$\text{As}\ \% = \frac{116{,}4[Vt_N - (t_x - t_B)]}{m}$$

$$\text{Sb}\ \% = \frac{189{,}25\ [Vt_N - (t_x - t_B)]}{m}$$

$$\text{Cu}\ \% = \frac{197{,}5\ [Vt_N - (t_x - t_B)]}{m}$$

dans lesquelles V est le volume de la solution de thiosulfate de sodium exprimé en ml, ajouté dans la solution à titrer et m est la masse du prélèvement analytique exprimé en microgrammes.

Elles ont été établies pour une intensité du courant d'électrolyse égale à 3 mA et les valeurs numériques suivantes des constantes Faraday = 96480C; As = 74,92; Sb = 121,7; Cu = 63,54.

RESULTATS ET CONCLUSIONS

Les méthodes coulométriques appliquées aux dosages microanalytiques de l'arsenic, de l'antimoine et du cuivre dans les substances organiques permettent de déterminer les teneurs centésimales de ces métaux avec la precision classique de la microanalyse organique élémentaire comme le montrent les tableaux I, II, et III.

Tableau I.—Arsenic

			Masses d'arsenic			
Substance	*m*, *mg*	As, % calculé	calculée *µg*	trouvée *µg*	As, % trouvé	Ecart As % tr.-As % calc.
Arséniate de sodium	2,107	24,00	506	503	23,0	−0,1
	3,485		836	834	23,9	−0,1
	2,311		555	559	24,2	+0,2
	4,010		962	966	24,1	+0,1
Acide benzène arsonique	3,070	37,08	1138	1134	36,9	−0,1
	3,583		1329	1332	37,2	+0,1
	4,183		1551	1549	37,0	−0,1
Acide arsanilique	2,249	34,51	776	775	34,5	0,0
	2,783		960	958	34,4	−0,1
	4,172		1440	1439	34,5	−0,0
	3,441		1187	1191	34,6	+0,1

Tableau II.—Antimoine

			Masses d'antimoine			
Substance	*m*, *mg*	Sb, % calculé	calculée *µg*	trouvée *µg*	Sb, % trouvé	Ecart Sb % tr.-Sb % calc.
Hémitrioxyde d'antimoine	2,511	83,53	2097	2097	83,5	0,0
	1,745		1458	1456	83,4	−0,1
	1,245		1036	1039	83,8	+0,3
	0,987		824	825	83,6	+0,0
Triphénylstibine	2,850	34,89	994	995	35,0	+0,1
	2,175		759	753	34,7	−0,2
	2,087		728	728	34,9	0,0
	2,034		710	707	34,8	−0,1
	2,264		790	785	34,6	−0,3

TABLEAU III.—CUIVRE

Substance	*m*, *mg*	Cu, % calculé	Masses de cuivre		Cu, % trouvé	Ecart Cu % tr.-Cu % calc.
			calculée *µg*	trouvée *µg*		
Sulfate de cuivre ($CuSO_4$, $5H_2O$)	3,719	25,45	946	950	25,5	+0,1
	4,709		1198	1197	25,4	0,0
	5,624		1431	1432	25,5	0,0
	7,015		1786	1785	25,4	0,0
	7,469		1900	1904	25,5	+0,1
Bis(phénylbutanedione 1,3) cuivre	2,716	16,47*	447	442	16,3	−0,2
	4,345		716	713	16,4	−0,1
	4,790		789	784	16,4	−0,1
	5,480		903	905	16,5	0,0

* Teneur certifiée de la substance fournie par le National Bureau Standard.

Les conditions opératoires décrites dans cette étude montrent qu'il est possible de doser avec la même précision chacun des éléments considérés pour des quantités comprises entre 3000 et 400 μg.

Facilement mises en oeuvre, ces méthodes coulométriques alliées éventuellement à d'autres méthodes analytiques s'avèrent des plus appropiées à la résolution de problèmes toujours plus complexes qui sont posés aux microanalystes.

Summary—A method is described for the microanalytical determination of arsenic, antimony and copper in organic compounds. These compounds are decomposed in a mixture of sulphuric and nitric acids. The decomposition products are then oxidized by hydrogen peroxide in the case of arsenic and by potassium permanganate in the case of antimony in order to obtain AsO_4^{3-} or SbO_4^{3-} ions respectively. In the case of copper, Cu^{2+} ions are obtained directly as a decomposition product. Iodine generated by constant-current electrolysis of potassium iodide contained in the solution is the titrating reagent, with sodium thiosulphate solution as intermediate reagent, and amperometric end-point detection. The iodine consumption is measured coulometrically.

Zusammenfassung—Ein Verfahren zur mikroanalytischen Bestimmung von Arsen, Antimon und Kupfer in organischen Verbindungen wird beschrieben. Die Verbindungen werden in einem Gemisch aus Schwefel- und Salpetersäure aufgeschlossen. Die Aufschlußprodukte werden im Falle von Arsen mit Wasserstoffperoxid, im Falle von Antimon mit Kaliumpermanganat zu AsO_4^{3-} bzw. SbO_4^{3-} oxidiert. Cu^{2+}-Ionen werden direkt als Aufschlußprodukt erhalten. Als Titrationsmittel dient Jod, das durch Elektrolyse bei konstantem Strom aus in der Lösung enthaltenem Kaliumjodid erzeugt wird, als Zwischenreagens Natriumthiosulfat; der Endpunkt wird amperometrisch ermittelt. Der Jodverbrauch wird coulometrisch gemessen.

BIBLIOGRAPHIE

1. G. Charlot, *Les méthodes de la Chimie Analytique*, Masson, Paris, 1956.
2. M. Bigois, *Talanta*, 1972, **19**, 147.
3. H. Lieb et O. Winstersteiner, cités par Pregl et Roth, *Quantitative organische Mikroanalyse*, 7e Auflage, p. 178, Springer, Wien, 1958.
4. E. W. Hammock, R. A. Brown et E. H. Swift, *Anal. Chim.*, 1948, **20**, 1048.
5. F. Pregl et R. Roth, *Quantitative organische Midroanalyse*, 7e *Auflage*, p. 25, Springer, Wien, 1958.
6. R. Rousselet et J. Canal, *Bull. Soc. Chim. France* 1964, **8**, 1852.
7. J. Cadersky, *Z. Anal. Chim.*, 1969, **244**, 122.

Talanta, 1972, Vol. 19, pp. 163 to 172. Pergamon Press. Printed in Northern Ireland

PRECONCENTRATION TECHNIQUES FOR TRACE ANALYSIS *VIA* NEUTRON ACTIVATION

J. MARK ROTTSCHAFER*
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

and

RONALD J. BOCZKOWSKI and HARRY B. MARK, JR.
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(*Received* 5 *July* 1971. *Accepted* 1 *October* 1971)

Summary—A review is given of the methods that have been proposed for enrichment of trace elements in samples that are to be analysed by neutron-activation methods. The emphasis is on classification of methods, with full illustrations by means of practical examples.

THE RECENT CONCERN over metal pollutants in the environment has resulted in increased efforts to develop satisfactory analytical procedures for determining trace metals in natural systems. The fact that many metals are found at low concentration levels in biological or other natural systems has imposed serious limitations on the analytical techniques that can be applied to direct determination of these trace metals.

Neutron-activation analysis (NAA), because of its inherent sensitivity, has become a prime technique for trace analysis.[1] The sensitivity of this technique for a number of elements is 1 part per milliard (ppM)[2,3] and under ideal conditions can be as low as one part in 10^{12}.[4] Despite this great sensitivity, the necessary procedures for using NAA for trace metal analysis will, in many cases, limit the actual concentration levels that can accurately be determined.

A good example of this is the use of NAA to determine metal ion concentrations in blood or sea-water samples where the metal species may be present in concentrations of 10^{-6}–$10^{-12}M$.[5,6] Since the metal or metals of interest are at such low concentrations, it is necessary to irradiate a large volume of sample in order to achieve a sufficient count rate. The bulk matrix, however, may absorb neutrons and thereby shield the trace elements of interest from activation.[7] Furthermore, the matrix itself may become highly radioactive and obscure the activity of the trace metals present. This latter fact is especially true for sea-water and biological samples in which large amounts of ^{24}Na are produced on irradiation. These various factors combine to reduce the sensitivity of NAA for trace metals in such systems.

One solution to such problems is to separate and isolate trace metals from the bulk matrix after irradiation. "Hot" chemical separation is a technique commonly employed to allow the determination of a metal when other interfering radionuclides may be present after irradiation.[6] While such a technique might be useful, there are significant difficulties associated with its use. Special facilities and equipment are required to handle radioactive samples for separation procedures. In the case of short-lived nuclides, the time required for chemical separation may be of such a length as to completely preclude the use of this technique.

An alternative procedure which has been effectively employed is to separate and

---

* Present address: BASF-Wyandotte Chemicals Corp., Wyandotte, Michigan 48192.

concentrate the desired species from the bulk matrix before irradiation. The problems of handling "hot" solutions are eliminated and the concentrated sample can more conveniently be determined by NAA. However, great care is necessary to avoid introducing impurities (at the level contained by the sample or even more) from reagents, etc, during the preconcentration procedure. Such preconcentration methods have been both widely and successfully used and are reviewed here.

Taylor[8] has discussed in detail several methods of preconcentration used in conjunction with NAA to analyse for trace elements in blood, cerebrospinal fluid and urine. Among the methods discussed were column chromatography, electrophoresis and ultracentrifugation. Joyner *et al.*[9] published a review and an evaluation of preconcentration methods used with a number of analytical techniques for the determination of trace metals in sea-water. These previous reviews have presented only a few examples of the application of preconcentration techniques to NAA. This paper is intended as a general review of the subject without including references cited in the reviews mentioned above.

CHROMATOGRAPHIC METHODS

Chromatographic methods are ideally suited for preconcentration and offer the added advantage of being able to isolate the concentrated species as pure components. The following describes the various chromatographic techniques that have been applied to the preconcentrating of species for determination by NAA.

Ion-exchange chromatography

Ion-exchange chromatography has been used extensively both alone and in conjunction with other techniques to concentrate and separate elements for NAA. In the biomedical field it has been used to determine protein-bound iodine in human blood and plasma. The usual technique involves passing the sample through an anion-exchanging resin[10] to remove inorganic iodide or through a mixed-bed resin[11] to remove iodide and non-protein-bound electrolytes. The effluent containing the protein-bound iodide is then irradiated and analysed. Hamada and co-workers[12] varied this procedure slightly by oxidizing the effluent with chromic acid and distilling the iodine produced into a potassium hydroxide solution. This solution was evaporated to dryness and the residue irradiated.

Total organic iodine,[13] free thyroxine[14] and total thyroxine[15] in human serum have been determined after separation by ion-exchange. Zaichik *et al.*[16] have designed a scheme for the determination of free iodide, and hormonal and non-hormonal iodide in blood serum. Free iodide is removed from the sample with Dowex-1 and eluted (A). Organic iodide is sorbed on Dowex 50. Non-hormonal iodide can be eluted from the resin with water (B) and hormonal iodide eluted with a buffer at pH 2 (C). Samples A, B and C are then lyophilized and irradiated.

Inorganic iodide has been separated from urine on an anion-exchanging resin.[17,18] In one example, the iodide can be selectively eluted for irradiation.[17] In another, after the elution of bromide and chloride ions, the resin is dried and irradiated directly.[18] Direct irradiation of the resin has also been applied to determine inorganic fluoride in urine.[19]

In another biochemical application,[20] selenocystathionine was extracted from nuts. The extract was passed through a Dowex-1 column and the fractions irradiated for determination.

Ion-exchange has been particularly useful in preconcentrating elements from natural water systems since essentially unlimited volumes can be passed through a column to obtain the desired sensitivity. Examples are given below.

Rubidium and caesium concentrations in the North Atlantic[21] and vanadium in the Colorado River[22] and in other natural water systems[23] have been determined by concentrating the elements on cation-exchanging resin. After elution from the column the sample is evaporated and irradiated. A similar technique has been used to determine silver ion present in samples of the rain water produced by cloud seeding with silver iodide.[24] A sensitivity of 10^{-10} g is reported. ^{230}Th and ^{232}Th have also been determined in natural water systems.[25] After cation-exchange concentration and elution with EDTA, the thorium is co-precipitated with titanium hydroxide for irradiation.

An anion-exchanging resin can be used for preconcentration of elements which form anionic complexes. Rhenium (as perrhenate ion) in sea-water,[26] and molybdenum and manganese present in solution as the molybdate and permanganate ions[27] have been determined by this method after elution from the column. Chromate ion in the ppM range in water[28] and mercury present in urine[29] have also been preconcentrated on anion-exchanging resin. In both cases the resin was irradiated directly without elution.

Similarly ion-exchanging membranes have been used as a preconcentration matrix for cations in aqueous solutions.[30–32] The procedure is to stir pieces of membrane in the solution, allowing sufficient time to reach equilibrium or to obtain sufficient metal concentration in the membrane for analysis. The membranes are then dried and irradiated. Green *et al.*[33] were able to determine ppM quantities of gold by using paper loaded with 50% Ionac SRXL resin (a resin specific for gold and the platinum group metals).

Paper chromatography

The technique of paper chromatography has also been widely used as a means of preconcentration. It offers an advantage in that the paper chromatogram containing the isolated species can itself be irradiated without further preparatory steps. This method has been notably successful in determining organic and biologically-related compounds.

While first row elements, such as hydrogen, carbon, oxygen, or nitrogen are not suitable for NAA, many of the organic and biologically related compounds contain elements such as sulphur, phosphorus, chlorine, or bromine that can be activated, and therefore be determined by NAA.

By this method phospholipids have been determined in human blood serum and spermatozoa,[34] in liver bile,[35] and in liver biopsy specimens and plasma.[36] Phospholipids have also been separated on paper and determined by NAA after extraction from cerebrospinal fluid and concentration on a silic acid column.[37] Strickland and Benson[38] were able to determine phosphatides after extracting them from cell fractions, converting them into phosphate diesters and separating them on paper. Phosphoryl peptides in protein[39] and mono- and oligonucleotides in calf thymus DNA and MS2-RNA have been determined after electrophoretic paper chromatography separation.[40] The purity of phosphate nutrient solutions for botanical use have even been determined with use of a paper chromatography preconcentration step.[41]

Schmeiser and Jerchel[42,43] have determined biologically-related compounds containing sulphur, chlorine, bromine and phosphorus. Skinner *et al.*[44] have determined chlorine- and bromine-containing drugs after separation and preconcentration by paper chromatography. Iodostyrine[45] and other iodo-compounds[46] in blood serum have been separated and determined. Certain organobromine compounds have been found in deproteinized spinal fluid.[47] Bromine analogues of DDT have also been separated for analysis.[48,49] Iodine and iodine compounds,[50] including isomers of di-iodobenzoles,[51] have been separated from aqueous solutions and determined by NAA.

If the compound to be determined does not contain an element suitable for activation, derivatives can be prepared which will contain a suitable nuclide. Steim and Benson[52] prepared bromine derivatives of amino-acids, carboxylic acids, keto-acids and sugars for paper chromatographic separation and irradiation. Unsaturated fatty acids in the form of mercury complexes have also been separated and determined by these authors.[52]

Metal ions and metal-containing compounds have also been isolated for analysis by paper chromatography. Cobalt and vanadium were determined on paper chromatograms after tissue samples were ashed, dissolved and chromatographed before NAA.[34] After homogenization and deproteinization of serum, muscle and liver tissue, selenomethionine was separated from other components and determined.[53] Sodium, uranium and the lanthanide elements have been separated by ascending paper chromatography on Whatman No. 1 filter paper with mixtures of alcohol and nitric acid to develop the chromatogram.[54,55] The chromatogram strips were irradiated for analysis.

Zinc[56] and magnesium[57,58] present in aqueous solutions were determined by NAA after chromatographic preconcentration. These metal ions were extracted from aqueous solutions into chloroform by complexation with 5,7-dibromo-8-hydroxyquinoline. The metal complexes were separated from excess of chelating agent by paper chromatography. Though zinc could be determined from the activity of the ^{65}Zn produced on irradiation, magnesium, having a low abundance of the isotope that can be activated and a low thermal neutron cross-section (^{26}Mg $= 11\%$, $\sigma = 0{\cdot}03$ barn),[59] could not be determined from ^{27}Mg. This difficulty was obviated by determining the activity of ^{82}Br produced (^{81}Br $= 50\%$, $\sigma = 3{\cdot}0$ barn)[59] when the magnesium complex was irradiated and hence indirectly the amount of magnesium present.

Miscellaneous chromatographic methods

Other chromatographic methods of preconcentration have also been applied to NAA. Column chromatography has been used to separate chlorine- and bromine-containing drugs[44] and to collect phospholipids extracted from cerebrospinal fluid.[37] Thin-layer chromatography has been used to separate mercurous and mercuric ions from other cations.[60] Following this, a section of the substrate containing these mercury species was taken for NAA.

Protein-bound elements have been separated from other materials present in blood serum by gel permeation chromatography. Fritze and Robertson[61] have determined a large number of protein-bound metals by freeze-drying the protein fraction of the eluate, irradiating and then either determining the activity directly or after a radiochemical separation. Protein-bound copper[62] and iodine[63] have also been preconcentrated for NAA by using gel permeation chromatography.

EXTRACTION METHODS

Solvent extraction has often been used as a means of preconcentration. Vanadium in blood samples[64,65] has been determined by extracting with 8-hydroquinoline, evaporating the solvent and irradiating the residue for analysis. Thenoyltrifluoroacetone has been used to extract calcium, copper, magnesium and manganese from serum[66] into a tetrahydrofuran/benzene solution. NAA of these metals was performed after re-extracting the metals into a small volume of nitric acid and irradiating. Selenium in biological materials[67] was isolated for analysis by first drying the sample and then oxidizing it with nitric acid and hydrogen peroxide and finally extracting the selenium with 8-mercaptoquinoline.

The use of solvent extraction in conjunction with other techniques for preconcentration has also been cited in the literature. As an initial step, before further fractionation, solvent extraction has been used to separate phospholipids from cerebrospinal fluid[37] and phosphatides from cell functions.[38] A determination of selenocystathionine in nuts[20] was obtained after an initial extraction followed by fractionation on an ion-exchange resin and irradiation.

Solvent extraction has proved to be useful in isolating metals from sea-water or aqueous solutions after chelation of the metal. Using sea-water samples, extractions have been made of copper, manganese and zinc with diethyldithiocarbamate into chloroform,[68,69] uranium with tri-n-octylphosphine oxide into cyclohexane[70] and vanadium with α-benzoinoxime into benzene.[71] In each case the solvent was evaporated and the residue irradiated for analysis. Zinc[56] and magnesium[57,58] were extracted from aqueous solutions into chloroform as the 5,7-dibromo-8-hydroxyquinolinates and separated from excess of chelating agent and solvent by paper chromatography before irradiation. In a similar application, a mercury dithizone complex was extracted into chloroform and the solution evaporated on plastic film which was irradiated directly.[72] This method appears to have the added advantage of preventing mercury volatilization losses since mercury tends to react with unsaturated bonds in the plastic film.[73]

Extraction methods can also be employed to remove impurities or interfering nuclides before determination. Uranium, for example, has been removed from solutions by complexing with tributyl phosphate and extracting. This allowed trace amounts of copper, cobalt and manganese in the original solution to be determined.[74]

PRECIPITATION METHODS

Both precipitation and co-precipitation have been used to remove trace elements from bulk solution. When irradiating a precipitate directly, it is necessary that neither the precipitating agent nor the co-precipitant contain nuclides with an activity which would interfere in the determination. A common procedure to circumvent this problem is the separation of the element of interest from the precipitate and its conversion into a form more suitable for analysis.

Rona *et al.*[75] coprecipitated manganese and zinc from sea-water with hydrous ferric oxide. After dissolution of the separated precipitate with hydrochloric acid, iron as the trichloride was removed from the solution by extracting with isopropyl ether. The aqueous phase was evaporated to dryness and the residue then irradiated and analysed. A similar procedure has been employed in the determination of ruthenium in sea-water.[76] After precipitation and extraction of the iron from the dissolved precipitate as described above, the hydrochloric acid solution is evaporated. The residue is redissolved in a potassium permanganate–sulphuric acid solution and from it ruthenium oxide is distilled into hydrochloric acid for subsequent irradiation and determination. The lanthanide elements have also been co-precipitated with hydrous ferric oxide.[77–80] After dissolution of the precipitate in hydrochloric acid and extraction of the iron, uranium and thorium are removed by anion-exchange and the eluate is evaporated for irradiation.

In a few instances it has been possible to irradiate the ferric hydroxide precipitates directly in order to determine co-precipitated metals without removal of the iron. This method has been applied to determine tantalum in sea-water,[81] thorium in mineral springs and Japanese coastal waters,[82] and indium in rain water.[83]

Calcium oxalate has been employed as a co-precipitant and used to precipitate barium and strontium from urine,[84] strontium from sea-water,[85] and several rare-earth elements from hot spring water.[86] After separation and drying, the precipitate was irradiated directly.

A number of instances have been reported of precipitating metal ions with an appropriate anion of a soluble salt. Cobalt, zinc and uranium in sea-water have been precipitated in this manner with disodium phosphate.[87] The precipitate was then dissolved in acid and passed through cation- and anion-exchanging columns to separate the metals for irradiation and NAA. Thorium in urine has been determined by adding ammonia solution to an acidified urine sample and irradiating the resultant precipitate.[88] By a precipitation method, uranium in milk has been determined to one part in 10^{12}.[89] The procedure entailed drying and ashing the milk, dissolving the residue in hydrochloric acid and precipitating the uranium with sodium ferrocyanide.

An unusual determination of ^{18}O in water has been accomplished by converting the oxygen into carbon dioxide and thence into solid ammonium carbonate which is irradiated.[90] With suitable modification, this method could be applied to the determination of tagged organic or biological materials in aqueous solutions.

DRYING AND ASHING METHODS

Perhaps the simplest methods of concentration are evaporation or freeze-drying of an aqueous sample and ashing of a solid sample. Evaporation and freeze-drying have been applied to the analyses of lake water,[91,92] sea-water,[93,94] mineral spring water[95] and Rhine river water.[96] Aluminium in reactor cooling water[97] and manganese in nitric and hydrochloric acids[98] have been determined by irradiating the residue after evaporation. Sodium and phosphorus have been determined in cervical mucus which has been dried and ashed.[99] Similar analyses have been reported for vanadium, arsenic, molybdenum, tungsten, rhenium and gold in dried marine organisms[100,101] and for gold in wine.[102]

Simple freeze-drying has been utilized to reduce sample size and to prevent the radiolysis of water present in a sample. Such a procedure facilitated the determination of selenium in eye lenses,[103] egg yolks[104] and sera and plasma,[105] of cadmium in biological tissue[106] and of bromine, chlorine, radium, mercury, chromium, phosphorus, rubidium, iron, cobalt and zinc in blood.[107] Freeze-drying has also been used as a final preconcentration step before irradiation of effluents from gel permeation[61] and ion-exchange chromatography[16] as cited above.

The methods of drying and ashing have certain disadvantages associated with their use. A sample, for example, may contain a species of interest that will volatilize during the drying or ashing process. A case in point is the determination of mercury and its compounds.[93] A recent paper,[72] however, reported a way to circumvent this problem. The procedure entailed the freeze-drying of an aqueous sample in a flask lined with a plastic film. The film itself was a convenient matrix for sample irradiation and good recovery of the mercury was reported as a result of the reaction of mercuric ion with unsaturated bonds present in the plastic film. Other problems associated with drying and ashing methods are cited in a paper describing the determination of several elements in sea-water.[93] Poor results were attributed to a combination of adsorption on storage container walls, interference from sodium and chloride gamma-spectra, and too rapid decay of short-lived nuclides.

ELECTROCHEMICAL METHODS

Electro-deposition is a very convenient way to concentrate trace metals for analysis. It offers the advantage of yielding a chemically and physically inert sample on a relatively small surface area that is suitable for analysis. Lux[108,109] initiated the idea of electrochemical preconcentration by the electrodeposition of silver on a rotating platinum disc electrode from a solution which also contained large amounts of cadmium. The deposited silver was irradiated and dissolved in *aqua regia* and a gamma-spectrum of the solution was taken. Direct counting of the silver film on the platinum electrode was not feasible, owing to the high background activity of the platinum itself. A relatively high background activity was also noted for the dissolved sample, owing to dissolution of some of the active platinum.

The problems associated with the use of a platinum substrate in NAA can be eliminated by choosing an electrode material that will not give rise to large interfering activity on irradiation. Such an approach was taken by Sion *et al.*[29] who determined mercury in aqueous solutions by electro-depositing it on aluminium wire. Since aluminium has a very short half-life, the electrode and deposited film could be irradiated directly and after approximately 30 min the mercury activity could be counted without background interference.

Pyrolytic graphite has also been used as an electrode material. Since pyrolytic graphite is totally carbon, it is not activated to yield a gamma-emitting isotope,[59] and since it can be obtained in a very pure form,[110] this substrate produces a very low background activity without any post-irradiation waiting period. Thus, counting can begin immediately after irradiation and even short-lived nuclides can be determined on this substrate. Several accounts of the application of this material to NAA have been published.[6,30–32,111–115]

MISCELLANEOUS METHODS

Other preconcentration techniques have also been reported. Sion *et al.*[29] have amalgamated mercury present in aqueous solutions on aluminium powder by stirring the powder in contact with the solution for several hours. After equilibrium has been achieved, the powder is filtered, dried and irradiated. After a brief waiting period, the activity of the aluminium declines and the mercury activity can be counted.

Total blood iodine[116] and protein bound iodine in serum[12] have been determined by NAA after oxidation of the sample and distillation from phosphoric acid solutions.

In biological materials the greatest potential interference for the NAA determination of trace metals is the presence of large amounts of sodium, potassium, chloride and bromide ions in the sample. These ions can be removed to an appreciable extent by dialysis of the sample. While heavy metals are usually complexed in biological materials, the uncomplexed interfering ions diffuse through the dialysis membrane, leaving the organically-bound heavy metals in the sample, which can then be irradiated. This technique has been used in the determination of manganese and copper in blood serum and cerebrospinal fluid,[117] protein-bound selenium in blood,[118] and brominated protein in serum.[119] Human serum has been dialysed before ion-exchange separation and irradiation for the determination of free thyroxine.[14]

Zusammenfassung—Es wird eine Übersicht über die Methoden gegeben, die zur Anreicherung von Spurenelementen in Proben für die Neutronenaktivierungsanalyse vorgeschlagen wurden. Der Nachdruck liegt auf der Klassifizierung der Methoden; praktische Beispiele dienen zur Illustration.

Résumé—On présente une revue des méthodes qui ont été proposées pour l'enrichissement d'éléments à l'état de traces dans des échantillons qui doivent être analysés par les méthodes par activation de neutrons. On insiste sur la classification des méthodes, avec illustrations complètes au moyen d'exemples pratiques.

REFERENCES

1. H. J. M. Bowen and D. Gibbons, *Radioactivation Analysis*, Clarendon Press, Oxford, 1963.
2. G. W. Leddicotte and S. A. Reynolds, *The Determination of Trace Elements by Neutron Radioactivation Analysis*, ASTM Bulletin, 1953, 29.
3. H. P. Yule, *Anal. Chem.*, 1965, **37**, 129.
4. A. A. Smales, in *Trace Analysis*, J. H. Yoe and H. J. Koch, Jr., eds., p. 518. Wiley, New York, 1957.
5. G. T. Seaborg and J. J. Livingood, *J. Am. Chem. Soc.*, 1938, **60**, 1784.
6. H. B. Mark, Jr., *J. Pharm. Belg.*, 1970, **25**, 367.
7. F. Girardi, *Talanta*, 1965, **12**, 1017.
8. D. M. Taylor, *Nucl. Activ. Tech. Life Sci., Proc. Symp.*, Amsterdam, 1967, p. 391.
9. T. Joyner, M. L. Heally, D. Chakrovarti and T. Koyanagi, *Environ. Sci. Technol.*, 1967, **1**, 417
10. E. M. Smith, J. M. Mozley and H. N. Wagner, Jr., *J. Nucl. Med.*, 1964, **5**, 828.
11. C. W. Tang and R. H. Tomlinson, *Nucl. Activ. Tech. Life Sci., Proc. Symp.*, Amsterdam, 1967, p. 427.
12. S. Hamada, K. Torizuka, K. Hamamoto, J. Nakagawa, T. Mori, R. Morita, T. Nakagawa, J. Kanishi, T. Miyake and M. Fukare, *Radioisotopes*, 1967, **16**, 14.
13. R. H. Tomlinson and M. W. Billingshurst, *Trans. Am. Nucl. Soc.*, 1969, **12**, 458.
14. S. Hamada, K. Torizuka, K. Hamamoto, T. Mori, R. Morita, T. Nakagawa and J. Kanishi, *Radioisotopes*, 1969, **18**, 354.
15. M. H. Feldman, J. McNamara, R. C. Rebra and W. Webster, *J. Nucl. Med.*, 1967, **8**, 123.
16. V. E. Zaichik, Y. Ryabukhin, A. D. Mel'nik and V. Cherkashin, *Med. Radiol.*, 1970, **15**, 33.
17. H. N. Wagner, Jr., W. B. Nelp and J. H. Dowling, *J. Clin. Invest.*, 1961, **40**, 1984.
18. D. J. Morgan, A. Black and G. R. Mitchell, *Analyst*, 1970, **94**, 740.
19. S. Ohno, M. Suzuki, K. Sasajima and S. Iwata, *ibid.*, 1970, **95**, 260.
20. G. J. Olivares, L. Aronow and F. Kendel-Vegas, *Acta Cient. Venez.*, 1967, **18**, 9.
21. A. A. Smales and L. Salmon, *Analyst*, 1955, **80**, 37.
22. K. D. Linstedt and P. Kruger, *J. Am. Water Works Assoc.*, 1969, **61**, 85.
23. *Idem, Anal. Chem.*, 1970, **42**, 113.
24. J. A. Warburton and L. G. Young, *J. Appl. Meteorol.*, 1968, **7**, 433.
25. H. G. Meyer, H. J. Born, H. Stärk and C. Turkowsky, *Radiochim. Acta.*, 1968, **10**, 128.
26. A. D. Matthews and J. P. Riley, *Anal. Chim. Acta*, 1970, **51**, 455.
27. V. Maxia, *Ric. Sci.*, 1959, **29**, 1476.
28. F. W. Lima and C. M. Silva, *J. Radioanal. Chem.*, 1968, **1**, 147.
29. H. Sion, J. Hoste and J. Gillis, *Microchem. J. Symp. Ser.*, 1962, **2**, 959.
30. U. Eisner, J. M. Rottschafer, F. J. Berlandi and H. B. Mark, Jr., *Anal. Chem.*, 1967, **39**, 1466.

31. U. Eisner and H. B. Mark, Jr., *Talanta*, 1969, **16**, 27.
32. H. B. Mark, Jr., U. Eisner, J. M. Rottschafer, F. J. Berlandi and J. S. Mattson, *Environ. Sci. Technol.*, 1969, **3**, 165.
33. T. E. Green, S. L. Law and W. J. Campbell, *Anal. Chem.*, 1970, **42**, 1749.
34. A. A. Benson, B. Marvo, R. J. Flipse, H. W. Yurrow and W. W. Miller, *Proc. 2nd. Int. Conf. Peaceful Uses Atomic Energy*, Geneva, 1958, paper 858.
35. F. Nakayama and R. Blomstrand, *Acta Chem. Scand.*, 1961, **15**, 1595.
36. R. Blomstrand and K. Nakayama, *Scand. J. Clin. Lab. Invest.*, 1962, **14**, 28.
37. *Idem*, *J. Neurochem.*, 1961, **8**, 230.
38. E. H. Strickland and A. A. Benson, *Arch. Biochem. Biophys.*, 1960, **88**, 344.
39. D. C. Shaw, *Nature*, 1967, **215**, 410.
40. G. W. Rushinzky and W. W. Miller, *Anal. Biochem.*, 1967, **20**, 181.
41. J. Lustinec, *Biol. Plant. Acad. Sci. Bohemoslov.*, 1960, **2**, 67.
42. K. Schmeiser and D. Jerchel, *Angew. Chem.*, 1953, **65**, 366.
43. *Idem*, *ibid.*, 1953, **65**, 490.
44. W. A. Skinner, M. A. Leaffer and R. M. Parkhurst, *J. Pharm. Sci.*, 1968, **57**, 338.
45. A. Dimitriadou, P. C. R. Turner and T. R. Fraser, *Nature*, 1963, **197**, 446.
46. R. P. Ouellette, J. F. Balcius and K. Zappinger, *Intern. J. Appl. Radiat. Isotop.*, 1966, **17**, 649
47. I. Yanagisawa and H. Yoshikawa, *Radioisotopes*, 1967, **16**, 554.
48. F. P. W. Winteringham, A. Harrison and R. G. Bridges, *Nature*, 1951, **167**, 106.
49. *Idem*, *Nucleonics*, 1952, **10**, 52.
50. H. J. Born and H. Stärk, *Atomkernenergie*, 1959, **4**, 286.
51. F. Baumgartner and A. Schon., *J. Chromatog.*, 1964, **13**, 266.
52. J. M. Steim and A. A. Benson, *Anal. Biochem.*, 1964, **9**, 21.
53. A. J. Barak and S. C. Swanberg, *J. Chromatog.*, 1967, **31**, 282.
54. T. Nascutiu, *Aced. Rep. Populare Romine, Studii Cercetoni Chim.*, 1962, **10**, 275.
55. *Idem*, *Rev. Roumaine Chim.*, 1964, **9**, 283.
56. L. T. Harmison, S. Lakshmanan and D. Duffey, *Trans. Am. Nucl. Soc.*, 1965, **8**, 86.
57. J. B. Smathers, D. Duffey and S. Lakshmanan, *Anal. Chim. Acta*, 1969, **46**, 9.
58. *Idem*, *Nucl. Appl. Technol.*, 1969, **7**, 84.
59. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, New York, 1967.
60. H. Seiler, *Helv. Chim. Acta.*, 1970, **53**, 1893.
61. K. Fritze and R. Robertson, *J. Radioanal. Chem.*, 1968, **1**, 463.
62. D. J. R. Evans and F. Klaus, *Anal. Chim. Acta*, 1969, **44**, 1.
63. J. C. Veselsky, M. Nedbalek and O. Suschny, *Intern. J. Appl. Radiat. Isotop.*, 1970, **21**, 225.
64. H. R. Lukens, K. Heydorn and T. Choy, *Trans. Am. Nucl. Soc.*, 1965, **8**, 331.
65. K. Heydorn and H. R. Lukens, *Danish AEC Riso Report* No. 138, 1966.
66. M. C. Haven, G. T. Haven and A. L. Dunn, *Anal. Chem.*, 1966, **38**, 141.
67. O. Veveris, S. H. Mihelson, Z. Pelekis, L. Pelekis and J. Toure, *Latv. PSR Zinat. Akad. Vestis. Fiz. Teh. Zinat. Ser.*, 1969, **2**, 25.
68. J. F. Slowey, D. Hedges and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-22660, 1960.
69. J. F. Slowey, *U.S. At. Energy Comm. Rept.*, TID-233295 Sect. 2, 1966.
70. J. C. White and W. S. Lyon, *Talanta*, 1965, **12**, 823.
71. R. Bock and B. Jost, *Z. Anal. Chem.*, 1970, **250**, 358.
72. J. G. Montalvo, Jr., D. P. Thibodeaux and E. Klein, *Anal. Chim. Acta*, 1970, **52**, 160.
73. S. T. Hirozawa, personal communication, 1970.
74. H. Marchant and F. Hecht, *Monatsh. Chem.*, 1964, **95**, 742.
75. E. Rona, D. W. Hood, L. Muse and B. Buglio, *Limnol. Oceanog.*, 1962, **7**, 201.
76. B. W. Dixon, J. F. Slowey and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-23295 Sect. 3, 1966.
77. D. W. Hayes, J. F. Slowey and D. W. Hood, *U.S. At. Energy Comm. Rept.*, TID-23295 Sect. 4, 1966.
78. O. T. Høgdahl, *NATO Research Grant* #203, Semiannual Progress Report #2, Oct. 1, 1965–Mar. 31, 1966.
79. *Idem*, *ibid.*, #4, Oct. 1, 1966–Mar. 31, 1967.
80. O. T. Høgdahl, S. Melson and V. T. Bowen, *Neutron Activation Analysis of Lanthanide Elements in Sea Water*, Advances in Chemistry Series #73, p. 308. R. F. Gould, Ed., American Chemical Society Publications, 1968.
81. H. Hamaguchi, R. Kuroda, R. Hoshara and T. Shimizu, *Nippon Genshiryoku Gakkaishi*, 1963, **5**, 662.
82. M. Osawa, O. Tokunaga, M. Itani and M. Sakanoue, *J. Nucl. Sci. Technol.*, 1966, **3**, 333.
83. K. S. Bhatki and A. N. Dingle, *Radiochem. Radioanal. Lett.*, 1970, **3**, 71.

84. G. E. Harrison and W. H. A. Raymond, *J. Nucl. Energy*, 1955, **1**, 290.
85. S. R. Rao, A. A. Khan and P. R. Kamath, *Nucl. Radiation Chem. Proc. Symp., Bombay*, 1964, p. 199.
86. T. Oda, *Radioisotopes*, 1969, **18**, 39.
87. G. R. Doshi, *Indian J. Chem.*, 1967, **5**, 580.
88. B. L. Twitty and M. W. Boback, *Anal. Chim. Acta*, 1970, **49**, 19.
89. H. Wiechen, *Milchwissenschaft*, 1970, **25**, 95.
90. W. H. Ellis, G. J. Fritz and G. G. Rocco, *Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis*, p. 248. Texas A and M Press, College Station, Texas, 1966.
91. J. Selz, W. Haerdi and D. Monnier, *Chimia*, 1963, **17**, 354.
92. A. Wyttenbach, *ibid.*, 1966, **20**, 119.
93. D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta*, 1965, **29**, 259.
94. D. Z. Piper and G. G. Goles, *Anal. Chim. Acta*, 1969, **47**, 560.
95. L. M. Mosulishvili, N. E. Kuchava and E. N. Ginturi, *Soobshch. Akad. Nauk. Gruz. SSR*, 1970, **59**, 93.
96. G. Schmidt, *Kernforschungzentrum Rept.*, KFK-863, 1968.
97. J. F. Emery and G. W. Leddicotte, *U.S. At. Energy Comm. Rept.*, CF-58-9-20, 1960.
98. W. Otwinowski and Z. Allina, *Nukleonika*, 1963, **8**, 411.
99. E. Odelblad, B. Westin and K. G. Malmfors, *Acta Radiol.*, 1958, **49**, 137.
100. R. Fukai and W. W. Meinke, *Nature*, 1959, **184**, 815.
101. *Idem Limnol. Oceanog.*, 1962, **7**, 186.
102. G. I. Beridze, G. R. Macharoshvili and L. M. Mosulishvili, *Radiokhimiya*, 1969, **11**, 726.
103. R. H. Filby and W. L. Yakely, *Radiochem. Radioanal. Lett.*, 1969, **2**, 307.
104. J. Cals, *Mater. Respub. Konf. Probl. "Mikroelem. Med. Zhivotnovod."*, *1st.*, 1968, M. Kruming, ed., p. 170. Baku, USSR, 1969.
105. B. Maziere, D. Comar and C. Kellershohn, *Bull. Soc. Chim. Fr.*, 1970, 3767.
106. K. W. Lieberman and H. H. Kramer, *Anal. Chem.* 1970, **42**, 266.
107. W. A. Haller, R. H. Filby and L. A. Rancitelli, *Nucl. Appl.*, 1969, **6**, 365.
108. F. Lux, *Radiochim. Acta*, 1962, **1**, 20.
109. *Idem*, *ibid.*, 1964, **3**, 50.
110. *General Electric Pyrolytic Graphite Engineering Handbook*, General Electric Corporation, Detroit, 1963.
111. H. B. Mark, Jr., and F. J. Berlandi, *Anal. Chem.*, 1964, **36**, 2062.
112. B. H. Vassos, F. J. Berlandi, T. E. Neal and H. B. Mark, Jr., *ibid.*, 1965, **37**, 1653.
113. B. H. Vassos, *Ph.D. Thesis*, University of Michigan, 1965.
114. H. B. Mark, Jr., F. J. Berlandi, B. H. Vassos and T. E. Neal. *Proc. 1965 Intern. Conf. Modern Trends in Activation Analysis*, p. 107. Texas A and M Press, College Station, Texas, 1966.
115. F. J. Berlandi, *Ph.D. Thesis*, University of Michigan, 1966.
116. C. Kellershohn, D. Comar and C. Lepoec, *Intern. J. Appl. Radiat. Isotop.*, 1961, **12**, 87.
117. E. L. Kanobrocki, T. Fields, C. F. Decker, L. F. Case, E. B. Miller, E. Kaplan and Y. T. Oester, *ibid.*, 1964, **15**, 175.
118. R. H. Tomlinson and R. C. Dickson, *Proc. 1965 Intern. Conf. Modern. Trends in Activation Analysis*, p. 66. Texas A and M Press, College Station, Texas, 1966.

Talanta, 1972, Vol. 19, pp. 173 to 179. Pergamon Press. Printed in Northern Ireland

SPEKTRALCHEMISCHE ANALYSENMETHODEN UNTER BENUTZUNG DER DREIPHASENSYSTEME DER EXTRAKTION

A. I. BUSEV, W. P. SHIWOPISZEW, B. I. PETROW und J. A. MACHNEW
Moskauer und Permer Universitäten, USSR.

(*Eingegangen am* 16. *April* 1971. *Angenommen am* 13. *September* 1971)

Zusammenfassung—Es wird ein neues Konzentrierungsverfahren für Elemente vor deren Spektralanalyse vorgeschlagen. Das Verfahren verkürzt wesentlich die Analysendauer und erhöht die Empfindlichkeit und Genauigkeit der Bestimmungen. Dem neuen Verfahren liegt die Eigenschaft des Diantipyrylmethans als Extraktionsmittel zugrunde, eine Entmischung des organischen Lösungsmittels in zwei Phasen während der Extraktion zu bewirken. In einer der Phasen, der sogenannten "dritten Phase", werden die zu extrahierenden Elemente bis auf 95–98% konzentriert. Das kleine Volumen der "dritten Phase" gestattet es, diese sofort auf die Elektroden zu bringen und dadurch solche langwierigen Operationen wie Verdampfung, Veraschen der Extrakte und Auffüllen der Elektroden vor der Spektralbestimmung zu vermeiden. Es sind spektralchemische Analysenmethoden mit genügender Selektivität und Empfindlichkeit für die Bestimmung von Hg, Sc, Sn, Cd, Bi, Zr, Hf ausgearbeitet worden (Nachweisgrenze 0,5–3 μg). Es wurde gezeigt, wie aussichtsreich das besagte Verfahren für die Konzentrierung von Mikromengen der Beimischungselemente bei der Analyse von Reinststoffen ist.

EINE HÖHERE EMPFINDLICHKEIT der Methoden der Spektralanalyse wird vor allem durch die Ausarbeitung von spektralchemischen Analysenmethoden erreicht, die die geringen Gehalte an Beimischungen von den Hauptbestandteilen durch Extraktion, Abscheidung auf einem Kollektor, Destillation u.a. abtrennen. Auf diese Weise wird der Gehalt der Beimischungselemente in den Konzentraten um einige Ordnungen erhöht.

Chemische Spektralanalysenmethoden besitzen aber einige Nachteile. Vor der Spektralanalyse wird das Konzentrat, z.B. das Extrakt, einer langwierigen Behandlung unterworfen, die aus Verdampfung, Veraschung, Verdünnung mit Graphit und Auffüllung der Elektroden besteht.

Eine wesentliche Vereinfachung und Beschleunigung der Analyse, eine höhere Genauigkeit und Empfindlichkeit der spektralanalytischen Bestimmungen wird durch Konzentrieren der Elemente mit Hilfe der Dreiphasensysteme der Extraktion ermöglicht.[1]

Solche Vorgänge wie die Entmischung der organischen Schicht und die Bildung von drei Phasen (zwei organische und eine wässerige) wurden bei der Extraktion der Elemente durch Diantipyrylmethan (DAM) und seine Homologen beobachtet. In einer der organischen Phasen, der sogenannten "dritten Phase," deren Volumen kaum einige Tropfen beträgt, werden die extraktionsfähigen Elemente praktisch vollständig (bis auf 95–98%) konzentriert. Für das Elementkonzentrat als dritte Phase sind keine langwierigen Operationen wie Trocknung und Veraschung nötig. Es kann unmittelbar auf die Elektroden gebracht werden. Dadurch wird die

Analysendauer wesentlich (2 bis 3 mal) verkürzt und die Genauigkeit sowie die Reproduzierbarkeit der Resultate erhöht.

Gegenwärtig wird DAM bereits für die Trennung und Bestimmung von über 30 Elementen des Periodischen Systems benutzt.[2–5] Trotz seiner allgemeinen Anwendbarkeit sind mit seiner Hilfe einige hoch selektive Verfahren für die Trennung der Elemente ausgearbeitet worden. So lassen sich damit, z.B., Zn–Cd, Sc–Seltene Erden, Se–Te, Sb–Bi, Co–Ni, Ga–In sehr leicht voneinander trennen.

Dieses Verfahren ermöglicht in der Spektralanalyse eine leichte und rasche Konzentrierung eines oder mehrerer der in Spuren vorhandenen Elemente, wenn als Hauptbestandteil ein analoges oder beliebig andere Elemente vorhanden sind, die unter den gegebenen Analysenbedingungen nicht mit dem DAM reagieren.

In manchen Fällen gestattet das DAM, große Gruppen von Elementen gleichzeitig zu konzentrieren, was sehr bequem ist, wenn Reinststoffe auf fremde Zusätze geprüft werden müssen. So lassen sich aus sauren Lösungen in Gegenwart von Rhoda-nid ionen über 20 Elemente (Fe, Cu, Co, Zn, Mo, W, Sn, Ti, Zr, Hf, Th, U, Ge, Sb, Bi, Ga, In, Hg, Nb, Se u.a.) gleichzeitig ausscheiden. Wenn also nur das Rhodanidsystem verwendet wird, kann man bereits die ganze Summe der genannten Elemente aus den zu prüfenden Objekten ausscheiden, die als Hauptbestandteile Magnesium, Aluminium, Chrom und andere Elemente anthalten, die sich mit DAM nicht extrahieren lassen.

In der vorliegenden Übersicht sind die Ergebnisse der unter Anwendung verschiedener Extraktionssysteme durchgeführten Bestimmungen der Elemente angegeben. Diese Beispiele zeigen, welch große Aussichten sich bei der Anwendung der Dreiphasensysteme für Konzentrierung und nachfolgende spektralanalytische Bestimmung geringer Mengen der Elemente ergeben. Besonders aussichtsreich sind diese Systeme bei der Analyse von Reinststoffen und Halbleitern.

RHODANIDSYSTEM

Bestimmung von Quecksilber, Scandium und Zinn

Die Gesetzmäßigkeiten der Extraktion von in Komplexen gebundenen Elementen mit Hilfe von DAM in dem Rhodanidsystem ist ausführlich beschrieben.[6–8] Nach ihrer Fähigkeit, extrahiert zu werden, sind die Elemente in eine bestimmte Reihenfolge, der "Rhodanidreihe," (d.H. nach der Abnahme deren Extrahierbarkeit) angeordnet, und zwar: Sn $>$ Zn $>$ Co $>$ Mo $>$ W $>$ Ga $>$ Fe $>$ In $>$ (Hf, Zr, Th, Ti, Hg, U, Sb, Bi) $>$ Sc $>$ V $>$ Cd $>$ Mn $>$ Be. In Klammern sind jene Elemente angegeben, deren gegenseitige Einordnung einige Schwierigkeiten bereitet, wegen eines starken und dabei nicht einheitlichen Einflusses der Rhodanidionenkonzentration, sowie der gewählten Arbeitsbedingungen auf die Vollständigkeit der Extraktion der Elemente.

Der Übergang von einem Zwei-Phasensystem zu einem System mit drei flüssigen Phasen wird mühelos erreicht, wenn das organische Lösungsmittel Chloroform durch ein Gemisch von Chloroform mit einem unpolaren Lösungsmittel wie Benzol ersetzt wird. Bei der Bildung solcher Systeme werden güngstige Voraussetzungen für die Extraktion der Elemente geschaffen. In der dritten Phase, die zu 40% aus dem Rhodanidsalz des Reagenzes besteht, ist eine hohe Konzentration zweier Komponenten vorhanden, die für die Komplexbildung sowie für die Extraktion unentbehrlich sind: diese Phase enthält einerseits Rhodanidionen, die für die Bildung von

Thiocyanato-metallanionen erforderlich sind, zum anderen hochmolekulare Ionen des Reagenzes, die mit diesen Anionen eine Reaktion eingehen.

Die Untersuchung der Dreiphasensysteme hat folgendes ergeben: obwohl die allgemeinen Gesetzmäßigkeiten der Extraktionsprozesse hier dieselben wie in den Zweiphasensystemen bleiben, treten jedoch einige interessante Eigenheiten auf. Dies hängt wahrscheinlich damit zusammen, daß in den Zweiphasensystemen die Konzentration der reagierenden Komponenten bedeutend geringer ist, als in den Drei-Phasensystemen.

Es ist vor allem notwendig zu betonen, daß die Zahl der extrahierbaren Elemente immer größer wird. Es ist bereits möglich, solche Elemente in die organischen Phasen überzuführen, für die die Bildung von Rhodanidkomplexe gar nicht spezifisch ist. Zu solchen Elementen gehören Beryllium, Aluminium, Nickel, Yttrium, Lanthanum und andere seltene Erden.

Als zweite Eigenart der Dreiphasensysteme ist eine ausgesprochen enge Beziehung zwischen der Vollständigkeit der Extraktion der Elemente und der Acidität des Mediums zu nennen. Elemente wie Aluminium, Yttrium, Lanthanum sind zwar aus den schwach-sauren Medien extrahierbar, es genügt aber, den Säuregehalt auf 2–3N zu steigern, um die Extraktion praktisch auf Null zu bringen. Dieses besondere Verhalten der Dreiphasensysteme läßt neue abgeänderte Verfahren zur Trennung der Elemente mittels Extraktion entstehen.

Um die Extraktion geringer Mengen, sowie Spuren von Elementen besser zu erforschen, wurde radioaktives Kobaltisotop verwendet. Die Untersuchungen haben ergeben, daß das Extraktionsprozent in der dritten Phase zusammen mit der zweiten Phase, wo auch geringe Mengen Kobalt extrahiert werden, insgesamt mehr als 99% beträgt. So hat man sogar bei der unter ziemlich extremen Bedingungen verlaufenden Extraktion—es wurde 1 μg ^{60}Co einem Liter 200 g Nickelchlorid enthaltender Lösung zugesetzt—in der wäßrigen Phase nur 0,001 μg ^{60}Co nachgewiesen.

Das Dreiphasen-Rhodanidsystem wurde zur Ausarbeitung eines hochempfindlichen Verfahrens für die Bestimmung geringer Mengen von Quecksilber, Scandium und Zinn verwendet.

Auf der Grundlage des Studiums der Bildungsbedingungen der drei flüssigen Phasen im Rhodanid-Extraktionssystem, der Verteilung des Quecksilbers, Scandiums und Zinns zwischen den Phasen in Abhängigkeit vom Säuregehalt des Mediums, der Konzentration der Rhodanidionen und der Zusammensetzung des organischen Lösungsmittels werden für das Konzentrieren von μg-Mengen dieser Elemente als Extraktionsmittel eine Lösung des DAM in einem Benzol–Chloroformgemisch (Volumenverhältnis 7:3) und als Vergleichselement Kobalt empfohlen. Das Kobalt wird dabei gemeinsam mit dem Quecksilber, Scandium und Zinn aus einer an Salz- oder Schwefelsäure 1–2N Lösung, die 4–5% Ammoniumrhodanid enthält, vollständig extrahiert.

Ausführung der Analyse

Die 2–50 μg Hg, Sc oder Sn enthaltende Einwaage wird in Salz oder Schwefelsäure gelöst. Die Lösung wird quantitativ in einen Scheidetrichter gebracht und eine Standardlösung von Kobalt als Vergleichselement (10 μg) zugegeben; danach werden Salz oder Schwefelsäure und eine 50%-ige Ammoniumrhodanidlösung zugesetzt, bis die wäßrige Phase bei einem Gesamtvolumen von 20–30 ml 1–2N an Säure und 5%-ig an Ammoniumrhodanid ist. Dann gibt man 15 ml Extraktionsreagenz (eine Lösung von 0,5 g DAM im 7: 3 v/v Benzol–Chloroformgemisch) hinzu. Die nach dem Schütteln und Absetzenlassen gebildete dritte Phase wird auf die Stirnflächen von 10 Kohlenelektroden gebracht. Die Elektroden werden an der Luft leicht getrocknet und die Spektren photografiert. Die optimalen Bedingungen für die Aufnahme der Spektren aller zu bestimmenden Elemente werden entsprechend den experimentellen Bedingungen ausgewählt und sind nach der Beschreibung der Methodik für die Abscheidung der Elemente mittels Extraktion angegeben.

Quecksilber, Scandium und Zinn lassen sich in verschiedenen Untersuchungsobjekten bestimmen, deren Hauptbestandteile Erdalkalien und Seltene Erden, Aluminium, Chrom(III), Nickel u.a. bilden. Von besonderem Wert ist die Möglichkeit, Scandium in Seltenen Erden zu bestimmen.

JODIDSYSTEM

Bestimmung von Kadmium und Wismut

Die Gruppe der im Jodidsystem extrahierbaren Elemente ist etwas anders als die der im Rhodanidsystem extrahierbaren; dies ermöglicht die Ausarbeitung neuer, abgeänderter Extraktionsverfahren für die Trennung der Elemente. So lassen sich bei der üblichen Analyse die Elemente Ga–In, Sc–Y, Zn–Cd u.a. leicht voneinander trennen.

Es wird beispielsweise ein Verfahren zur Bestimmung von Mikromengen von Kadmium und Wismut angegeben.[9]

Um die optimalen Bedingungen für die Abscheidung von Kadmium und Wismut in dem Dreiphasensystem der Extraktion auszuarbeiten, wurde der Einfluß der Azidität des Mediums, Konzentration der Jodid-Ionen, Volumenverhältnis der wäßrigen zur organischen Phase, Zusammensetzung des organischen Lösungsmittels, Reagenzmenge u.a. untersucht.

Es wurde festgestellt, daß die Extraktion aus den schwefelsauren Lösungen vorgenommen werden muß; dabei darf die Konzentration der Schwefelsäure nicht unter $0{,}5N$ sinken. Das Lösungsmittel stellt ein Benzol–Chloroformgemisch dar (Volumenverhältnis 7:3). Als Vergleichselement ist Quecksilber vorgeschlagen, das sich aus einer $0{,}5N$-schwefelsauren Lösung zusammen mit Kadmium und Wismut extrahieren läßt. Zwecks vollständiger Extraktion verwendet man 0,5 g DAM. Das Volumen der "dritten Phase" wird nach dem Reagenzgehalt ermittelt, wobei immer dieselbe Menge DAM eingesetzt wird, um ein konstantes Volumen der Phase zu erhalten.

Für die Analyse wird eine 2–100 μg Cd oder Bi enthaltende Einwaage (0,5–1,0 g) in Schwefelsäure gelöst. Die Lösung wird quantitativ in einen Scheidetrichter gegeben, eine Standardlösung von Quecksilber (44 μg) und Schwefelsäure hinzugesetzt, wobei die Konzentration der letzteren bei dem Gesamtvolumen der wäßrigen Phase von 20–30 ml nicht unter $0{,}5N$ sinken darf. Es wird Kaliumjodid hinzugegeben, damit dessen Konzentration in der Lösung 5–6% beträgt, darauf werden 0.1 g Ascorbinsäure und 15 ml Lösung von 0,5 g DAM in 7:3 v/v Benzol-Chloroformgemisch hinzugefügt. Man schüttelt mindestens 15 min (bei kürzerer Schütteldauer ist die Extraktion der Elemente unvollständig), läßt die Entmischung der Phasen zustandekommen und bringt die "dritte Phase" tropfenweise auf die Kohlenelektroden.

Die Bestimmung von Kadmium und Wismut wird nicht durch Fe, Mn, Al, Mg, Cr, Ni, Be, Ga, La, Ce und andere Seltene Erden gestört.

NITRATSYSTEM

Bestimmung von Zirkonium und Hafnium

Aus den nitrathaltigen Medien kann durch DAM nur eine beschränkte Gruppe von Elementen (Zr, Hf, Sc, U, Bi, Hg) extrahiert werden.[10] Dies veranlaßt zur Ausarbeitung einer Reihe von hochselektiven Analysenmethoden.[11,12] Es muß betont werden, daß es in manchen Fällen sogar im Rahmen eines einzigen Extraktionsystemes gelingt, zusätzliche Trennungen durch Regulieren der Konzentration der Salpetersäure zu verwirklichen. So führt die Steigerung der Konzentration von Salpetersäure in der wäßrigen Phase auf $6N$ zu einem praktisch vollständigen

Übergang von Zirkonium und Hafnium in die Schicht des organischen Lösungsmittels, bei Scandium dagegen zur Einstellung der Extraktion.

Um die optimalen Bedingungen für die Abscheidung von Zirkonium und Hafnium in dem Dreiphasen-Extraktionssystem auszuarbeiten, wurde der Einfluß der Acidität des Mediums, des Volumenverhältnisses der wäßrigen und der organischen Phasen, die Zusammensetzung des Lösungsmittels und die Reagenzmenge untersucht.[13]

Eine möglichst vollständige Konzentrierung der Elemente in der "dritten Phase" findet statt, wenn als organisches Lösungsmittel ein Benzol–Chloroformgemisch im Volumenverhältnis 7:3 verwendet wird. Die Extraktion muß aus Lösungen, die mindestens 6*N* an Salpetersäure sind, vorgenommen werden. Die Anwesenheit von Chloriden und Sulfaten ist unerwünscht, weil durch Chloridionen die Zahl der extrahierbaren Elemente größer wird, die Gegenwart von Sulfaten aber zur Maskierung von Zirkonium und Hafnium, sowie des Vergleichselements Thorium führt. Letzteres läßt sich mit den zu bestimmenden Elementen abscheiden und muß der zu analysierenden Lösung unmittelbar vor der Extraktion zugesetzt werden.

Die zu analysierende 5–300 μg Zr oder 9–600 μg Hf enthaltende Lösung wird in einen Scheidetrichter gegeben, dann 2 ml 5×10^{-4} *M* Lösung von Thoriumnitrat (264 μg Th) und Salpetersäure hinzugefügt, bis die Azidität 6*N* ist, wobei sas Gesamtvolumen der wäßrigen Phase 15–30 ml beträgt; darauf werden 10 ml 4%-iger Lösung von DAM im organischen Lösungsmittel zugesetzt. Man schüttelt den Inhalt des Trichters 20–25 min, läßt die Entmischung der Phasen zustandekommen und bringt dann die "dritte Phase" auf die Elektroden. Über die Selektivität des Verfahrens kann man an Hand der Tabelle I urteilen.

SPEKTRALANALYTISCHE BESTIMMUNG DER ELEMENTE

Die Elementenkonzentrate als "dritte Phase" wurden nach dem Auftragen auf die Elektroden und Trocknung an der Luft der Spektralanalyse unterworfen. Als Lichtquelle diente der Funke, weil in dieser Lichtquelle der Effekt der gegenseitigen Beeinflussung der Elemente minimal ist.[14,15] Wesentlich für die Funkquelle ist nur die Molekularform, in der das Element in den zu analysierenden Untersuchungsobjekten vorliegt. Bei der Extraktion mittels DAM entstehen strukturell gleichartige Elementkomplexe, so daß es möglich wird, durch kombinierte Ausnutzung des Funkens und der DAM-Extraktion, den nicht unbedeutenden Einfluß der Molekularform der Verbindungen auf die Genauigkeit der Analysenergebnisse zu beheben. Eine größere Genauigkeit und höhere Empfindlichkeit der empfohlenen Methoden wird auch bei dem Auftragen der "dritten Phase" auf mehrere Elektroden (10–12) und deren nachfolgendem Photographieren auf dasselbe Spektrum erreicht (je 10

TABELLE I.—CHARAKTERISTIK DER SPEKTRALCHEMISCHEN VERFAHREN FÜR DIE BESTIMMUNG DER ELEMENTE UNTER ANWENDUNG DER DREIPHASENSYSTEME

Extraktions system	Das zu bestimmende Element	Matrix	Absolute Empfindlichkeit, μg	Standardabweichung, %
1. Rhodanid system	Hg	Be, Mg, Al	2,0	11,2
	Sc	La, Ni, Cr	2,0	9,0
	Sn		4,0	5,0
2. Jodid system	Cd	Fe, Cr, Co	1-3	13,0
	Bi	Ni, Mn, Al, Zn, Ga		14,0
3. Nitrat system	Zr	Sc, Y, La, Ce	5,0	5,6
	Hf	Al, Be, Mg In Ga, Cu, Zn, Cd	9,0	7,4

bei der Bestimmung von Hg, Sc, Sn, Cd oder Bi und je 12 für Zr und Hf). Die Spektren wurden mit dem Spektrografen ISP-28 photographiert; die Spaltbreite betrug, 0,01 mm; der analytische Abstand, 3 mm; Belichtungsdauer, 20 sec (15 sec bei der Bestimmung von Hg, Sc, Sn). Anregungsquelle: Generator IG-3, einfaches Schema, V = 200 V, I = 2,6 A (und 3,0 A bei der Bestimmung von Quecksilber, Scandium und Zinn) C = 0,02 μF, L = 0,15 mH.

Für die Aufnahme der Eichkurven werden bekannte Mengen der Elemente extrahiert. Die Berechnung des Durchschnittwertes wird auf Grund von 10–15 Spektren durchgeführt. Um verschiedene Einwaagen je nach dem Gehalt der Elemente in den Proben ausnutzen zu können, werden die Eichkurven anhand folgender Koordinaten zusammengestellt: die Differenz zwischen der Schwärzung des zu bestimmenden Elementes und des Vergleichselementes, und Logarithmus der absoluten Menge des zu bestimmenden Elementes in Mikrogramm. Als analytische Paare gelten folgende Linien:

Das zu bestimmende Element	Vergleichselement
Hg 253,65 nm Sc 255,23 nm Sn 283,99 nm	Co 241,16 nm
Cd 226,50 nm Bi 293,83 nm	Hg 253,65 nm
Zr 267,86 nm Hf 263,87 nm	Th 287,04 nm

Um klarzustellen, ob es möglich ist, Elemente in verschiedenen Untersuchungsobjekten zu bestimmen, wurden bei der Bildung der Eichkurven für die Bestimmung von Kadmium und Wismut als Grundlage Zink, Chrom, Mangan, Eisen, Kobalt und Nickel genommen; für die Bestimmung von Zirkonium, Hafnium, u.a. werden Scandium, Yttrium, Lanthan, Cer, Aluminium, Beryllium, Magnesium als Grundlage genommen. Meistenteils ist der Einfluß der Grundlage unbedeutend und für die Bestimmung von Hg, Sc, Sn, Cd, Bi, Zr und Hf kann man einheitliche Eichkurven benutzen, die nach synthetischen Etalons gebildet sind.

Die Methoden sind hochempfindlich und liefern gut reproduzierbare Resultate (Tabelle I).

Summary—A new method for concentrating elements before their determination by spectrography is described, which achieves considerable saving in time and improvement in sensitivity and accuracy. The method depends on the separation of a mixed organic solvent into two phases when diantipyrylmethane is present as extracting reagent. In one of the phases—the so-called "third phase"—the extracted elements are concentrated in 95–98% yield. The small volume of the third phase permits it to be transferred quantitatively directly to the electrode and so to dispense with time-consuming evaporation and ashing procedures before the spectrographic determination. Spectrochemical methods with adequate selectivity and sensitivity for the determination of Hg, Sc, Sn, Cd, Bi, Zr and Hf have been developed. The new procedure is shown to be very promising for the concentration of traces and the analysis of high-purity materials.

Résumé—On décrit une nouvelle méthode de concentration des éléments avant leur détermination par spectrographie, qui mène à un gain de temps considérable et à une amélioration de la sensibilité et de la précision. La méthode repose sur la séparation d'un solvant organique mixte en deux phases lorsque le diantipyrylméthane est présent en tant que réactif d'extraction. Dans l'une des phases—dénommée "troisième phase"—le séléments extraits sont concentrés avec un rendement de 95–98%. Le petit volume de la troisième phase lui permet d'être transférée quantitativement directement à l'électrode et d'éviter ainsi les longues techniques d'évaporation et d'incinération avant le dosage spectrographique. On a élaboré des méthodes spectrochimiques de sélectivité et sensibilité convenables pour le dosage de Hg, Sc, Sn, Cd, Bi, Zr et Hf. On montre que la nouvelle technique est très intéressante pour la concentration de traces et l'analyse de produits de haute pureté.

LITERATUR

1. W. P. Shiwopiszew, I. N. Ponosow und E. A. Selesnewa, *Zh. Analit. Khim.*, 1963, **18,** 1432.
2. W. P. Shiwopiszew, *Dokl. Akad. Nauk SSSR*, 1950, **76**, 1198
3. A. I. Busew, W. K. Akimow und S. I. Gusew, *Uspekhi Khim.*, 1965, **34**, 565.
4. W. P. Shiwopiszew, A. A. Minin, L. L. Miljutina, E. A. Selesnewa und W. H. Aitowa, *Tr. Kom. Analit. Khim. Akad. Nauk SSSR*, 1963, **14**, 133.
5. W. P. Shiwopiszew, *Zavodsk. Lab.*, 1965, **31**, 1043.
6. W. P. Shiwopiszew, I. N. Ponosow und B. I. Petrow, *Utschen. Sapiske Permsl. Univ.*, 1966, **141**, 3.
7. W. P. Shiwopiszew, W. S. Minina und B. I. Petrow, *Zh. Analit. Khim.*, 1967, **22**, 495.
8. W. P. Shiwopiszew, B. I. Petrow und I. N. Ponosow, *Radiochimiya*, (im Druck).
9. W. P. Shiwopiszew, Ju. A. Machnew und B. I. Petrow *Zh. Priklad. Khim.*, *Spektroskop.*, 1969 **11**, 779.
10. W. P. Shiwopiszew, L. P. Pjatossin und N. F. Sibirjakow, *Utschen. Sapiske Permsk. Univ.*, 1966, **141**, 194.
11. W. P. Shiwopiszew und L. P. Pjatossin, *Zh. Analit. Khim.*, 1967 **22**, 70.
12. W. P. Shiwopiszew und B. I. Petrow, *ibid.*, 1968, **23**, 1634.
13. W. P. Shiwopiszew, Ju. A. Machnew, B. I. Petrow und O. I. Sawina, *Zavodsk. Lab.*, 1969, **35**, 902.
14. Ju. A. Machnew, *Utschen. Sapiski Permsk. Univ.*, 1961 **19**, 125.
15. *Idem*, *ibid.*, 1963, **25**, 60.

Talanta, 1972, Vol. 19, pp. 181 to 195. Pergamon Press. Printed in Northern Ireland

INTERFERENCES AND THEIR ELIMINATION IN THE DETERMINATION OF THE NOBLE METALS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

R. C. MALLETT, D. C. G. PEARTON, E. J. RING and T. W. STEELE
Analytical Division, National Institute for Metallurgy, Johannesburg

(*Received* 10 *March* 1971. *Accepted* 7 *July* 1971)

Summary—A number of serious interferences in the determination of the noble metals by atomic-absorption spectrophotometry have been investigated, and ways of eliminating them considered. The use of the nitrous oxide and acetylene flame reduced many of the interferences but also reduced the sensitivity. Additions of lanthanum, copper sulphate, copper + cadmium sulphate, uranium, and vanadium as releasing agents were effective in the removal of interferences for one or more of the noble metals in the air-acetylene flame. Uranium additions were found to be effective in removing mutual interferences associated with the noble metals (osmium and iridium were not tested) whereas vanadium removed mutual and base-metal interferences. The precision and accuracy of methods of analysis based on the use of uranium and vanadium were acceptable, and the application of these methods to the analysis of noble metals collected by various procedures is briefly discussed.

ATOMIC-ABSORPTION SPECTROSCOPY (AAS) was considered to be a suitable technique for the determination of noble metals. However, a survey of earlier studies indicated that the determinations were subject to many interferences, arising from the noble metals themselves (mutual interference) and also from other metals or non-metals. Some investigators have made use of releasing agents for the removal of interferences; others have resorted to the use of hot flames.

Strasheim and Wessels,[1] using a butane–propane–air flame, found that platinum and rhodium were particularly subject to interferences. They were able to remove mutual interference with platinum by the addition of copper sulphate, but rhodium had to be determined by the standard addition technique. Measurements were made on 10% hydrochloric acid media. Palladium and gold were not subject to serious mutual interference but the acidity (10% hydrochloric acid) had to be closely controlled. Base metals had to be separated before the measurement of the noble metals.

Van Loon[2] determined platinum, palladium and gold in silver assay beads and found that addition of lanthanum (1%) removed the interferences encountered. Measurements were made on a 6*M* hydrochloric acid medium, and it was noted that the lanthanum had caused an enhancement in the adsorption measurement of the various metals.

Schnepfe and Grimaldi,[3] in the determination of palladium and platinum, found that mutual and base-metal interferences were removed by the addition of a mixture of copper and cadmium sulphates.

Scarborough[4] reported that when uranium was present no interferences were encountered in the determination of molybdenum, ruthenium, palladium and rhodium and there was also an enhancement in the absorption measurement of the noble metals.

Many interferences that occur in the cooler flames can often be reduced or eliminated by the use of hotter flames. Atwell and Hebert[5] found that many of the interferences encountered with the air–acetylene flame when rhodium was being determined were not present when the nitrous oxide–acetylene flame was used.

Up to the present no suitable methods whereby all the noble metals can be determined in one solution have been reported. It was therefore decided to try to determine as many noble metals as possible in a single solution, and this paper describes the investigations into the determination of platinum, palladium, rhodium, ruthenium and gold, the interferences encountered, and the methods used to eliminate these interferences. Preliminary investigations had indicated that osmium and iridium would not be present in the materials to be analysed at levels suitable for atomic-absorption measurement, so these were not included in this investigation.

EXPERIMENTAL

Apparatus

Spectrometer. A Techtron AA4 spectrophotometer with a Dl-20 digital indicator or the normal meter indicator unit, and Varian-Techtron hollow-cathode lamps were used. The wavelengths, slitwidths, and operating lamp currents are shown in Table I.

TABLE I.—INSTRUMENTAL PARAMETERS FOR THE TECHTRON AA4 SPECTOPHOTOMETER

Parameter	Pt	Pd	Rh	Ru	Au
Wavelength, *nm**	265·9	244·8	343·5	349·9	242·8
Spectral band width, *nm*	0·17	0·17	0·17	0·33	0·33
Lamp current, *mA*	10	7	5	10	4
Flow-rate, *l. min*$^{-1}$	1·75	1·75	2·25	3	1·75

* The most sensitive lines were used.

Flame. Most of the investigational work was carried out with the air–acetylene flame and a Techtron 0·10-m grooved burner. Maximum sensitivity for platinum, palladium and gold was observed when a lean flame was used. Rhodium required a normal flame, and ruthenium a rich flame.

In the tests where the nitrous oxide–acetylene and air–acetylene flames were compared, the Techtron 60-mm grooved burner was used for all measurements. To obtain maximum sensitivity, the procedure adopted was to set the flow-rates of the air and nitrous oxide to those indicated in Fig. 2 and then, while a solution was being aspirated, to adjust the acetylene flow for maximum sensitivity. This often resulted in a very lean flame, but care was taken not to reduce the acetylene flow to the point where a flash-back might occur.

Reagents

Standard noble metal solutions. Stock solutions of platinum, palladium and gold were prepared by the dissolution of the individual noble metals in *aqua regia.* The nitrate was removed from platinum and platinum solutions by repeated evaporations with hydrochloric acid. Gold solutions were not treated in this way because gold can be easily reduced with this treatment. When nitrate-free gold solutions were required, they were made from "Specpure" ammonium chloroaurate (NH_4AuCl_4) dissolved in hydrochloric acid. The stock solutions of rhodium and ruthenium, and of osmium and iridium, when used, were made from the "Specpure" ammonium chloro-salts (previously assayed gravimetrically, except for osmium) dissolved in hydrochloric acid.

Uranium solution (1 ml ≡ 250 mg of U). Dissolve 29·5 g of pure U_3O_8 in 40 ml of nitric acid (1 + 1). Evaporate to dryness, dissolve in nitric acid, hydrochloric acid, or *aqua regia* as required, and dilute to 100 ml. (if solutions free from excess of nitric acid are required, evaporate several times with hydrochloric acid.)

Vanadyl chloride ($VOCl_2$) *solution* (1 ml ≡ 100 mg of V). Although this reagent can be purchased it was prepared in the laboratory in the following manner. To 8·39 g of V_2O_5 (analytical grade) add 50 ml of comc hydrochloric acid. Heat the mixture gently until the initial reaction ceases, then boil for 10 min. Add hydrazine hydrochloride solution dropwise to the boiling solution until the green colour disappears, indicating complete reduction to blue vanadyl chloride ($VOCl_2$). Evaporate the solution to 25 ml and dilute it to 50 ml with water.

Interference studies

Noble metals can be collected by several procedures, *e.g.*, assay fusion with lead, nickel sulphide, or tin as the collectors. Solutions of prills obtained by assay fusion with lead as a collector, followed by cupellation, would not contain appreciable amounts of base metals, whereas the solutions of noble metals resulting from the other collection procedures, or solutions obtained from the chlorination of the ore would contain large amounts of base metals and their salts. Because the materials could be divided into two categories according to the type of interferences likely to be encountered, *viz.* mutual and base-metal interferences, it was decided to study these separately, and, if necessary, use different methods to control them.

In terference effects were recorded by comparison of the absorption of solutions containing the noble metals, either present together or added individually, depending on the nature of the test, with the absorption of similar solutions in the presence of the interfering ion. The concentrations of acids and releasing agents when used were the same in the test and the reference solutions and both sets of solutions were measured under the same operating conditions.

RESULTS

Mutual interference

Mutual interferences of the noble metals, tested in 4% *aqua regia** and in 10% hydrochloric acid media are shown in Tables II and III where the seriousness of these interferences in very evident. Further evidence of mutual interference in 4% *aqua regia* can be seen in Fig. 1*a*–1*f* where the effect of one noble metal upon another is shown.† Although ruthenium, osmium and iridium were added (Table II) these were not measured in the 4% *aqua regia* medium because they were present at too low a concentration. From a comparison of Tables II and IV it appears at first sight that the interferences suffered by platinum and rhodium were more severe in 10% hydrochloric acid medium than in 4% *aqua regia*, a feature that may be associated with the relatively large amount of ruthenium present in the former medium. Figures 1*b* and 1*c* indicate that ruthenium in 4% *aqua regia* depresses the absorption of platinum and rhodium. A similar effect can therefore be expected in a hydrochloric acid medium. The absorption of ruthenium was itself enhanced in both a 4% *aqua regia* medium. (Fig. 1*e*) and a 10% hydrochloric acid medium (Table III) by the presence of relatively large amounts of gold. Gold in a 4% *aqua regia* solution had a similar effect on rhodium (Fig. 1*f*).

It is evident that the phenomenon of mutual interference is a very complex one and it was necessary therefore to find methods whereby it could be removed or at least controlled.

Experiments with the nitrous oxide–acetylene flame. Since Atwell and Hebert[5] reported that the interferences encountered in the air–acetylene flame when rhodium was being determined were not present in the nitrous oxide–acetylene flame, it was decided to test this flame for the measurement of the other noble metals. It was obvious that this flame, when used normally, lowered the sensitivity for rhodium, so arrangements were made to introduce air to modify the characteristics of the flame. It can be seen from Table IV and Fig. 2 that, although there was an improvement in the recovery of platinum and rhodium with an increase in the nitrous oxide content of the gas mixture, there was a progressive decrease in sensitivity for all the noble metals except ruthenium. Little improvement in recovery was observed for ruthenium over that obtained with the air–acetylene flame. The mutual interference with gold caused a higher absorption; with palladium there was no effect from interferences either in the nitrous oxide *or* the acetylene flame.

Experiments on the use of releasing agents

A number of recommended releasing agents were examined, *viz.* copper sulphate,[1] lanthanum,[2] copper sulphate plus cadmium sulphate,[3] and uranium.[4] Where possible, the reported methods were adhered to. An exception was the substitution of the

---

* A 4% *aqua regia* solution is a solution containing 3 ml of hydrochloric and 1 ml of nitric acid, diluted to 100 ml with water.

† Although all the noble metals, with the exception of osimum and iridium, were tested in this way, only a few are shown, to serve as an example.

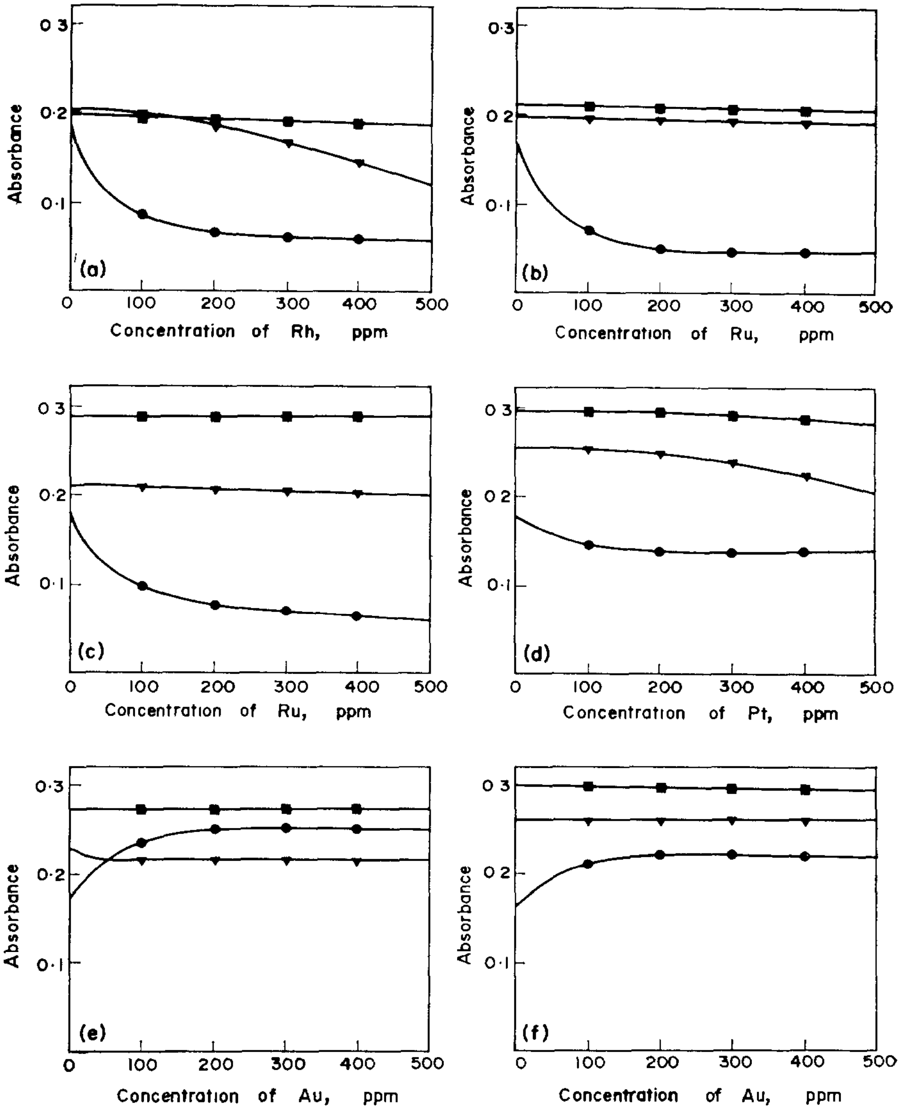


Fig. 1.—Mutual interference effects.

● 4% *aqua regia* only.

■ 4% *aqua regia* with 1% of U present.

▼ 20% $HClO_4$, 5% HCl with 1% of V present.

(*a*) Effect of Rh on 50 ppm of Pt.
(*b*) Effect of Ru on 50 ppm of Pt.
(*c*) Effect of Ru of 5 ppm of Rh.
(*d*) Effect of Pt of 5 ppm of Rh.
(*e*) Effect of Au on 30 ppm of Ru.
(*f*) Effect of Au on 5 ppm of Rh.

TABLE II.—MUTUAL INTERFERENCE OF THE NOBLE METALS IN 4% *aqua regia* SOLUTION

	Pt		Pd		Rh		Ru		Au		Ir		Os	
Solution	add.	rec.	add.	rec.	add.	rec.	add.	rec.	add.	rec.	add.	rec.	add.	rec.
I	120	100	20	20	5	4·1	5		5	5·05	1		1	
II	120	103	20	20	5	4·1	5		5	4·95	1		0	
III	120	103	20	20	5	4·1	5		5	5·05	0		1	
IV	120	101	20	20·2	5	4·1	0		5	5·05	1		1	
V	120	110	20	20·2	0		5		5	5·05	1		1	
VI	120	100	20	20	5	4·1	5		0		1		1	
VII	120	103	0		5	4·1	5		5	5·05	1		1	
VIII	0		20	20·2	5	5	5		5	5·05	1		1	

Throughout, add. = added, *ppm* and rec. = recovered, *ppm*.

TABLE III.—MUTUAL INTERFERENCE OF PLATINUM, PALLADIUM, RHODIUM, RUTHENIUM AND GOLD IN 10% HYDROCHLORIC ACID SOLUTION

	Pt		Pd		Rh		Ru		Au	
Solution	add.	rec.	add.	rec.	add.	rec.	add.	rec.	add.	rec.
I	60	26·2	15	14·8	8	4·8	150	177	20	20·8
II	100	57	15	14·8	3·2	1·8	150	189	20	20·1
III	100	55	6	5·9	8	4·7	150	186	20	19·5
IV	100	70	15	14·9	8	5·9	60	92	20	19·3
V	100	55	15	14·6	8	4·7	150	186	8	8·11

TABLE IV.—THE EFFECT ON THE MUTUAL INTERFERENCE OF THE NOBLE METALS OF VARYING THE RATIO OF THE AIR TO NITROUS OXIDE, WITH ACETYLENE AS THE FUEL GAS

		Recovery, %									
Air	Nitrogen	Pt		Rh		Pd		Ru		Au	
l/min	*l/min*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
5	0	70	63	77	68	101	99	140	137	100	100
3½	1	87	74	88	81	100	99	140	139	101	105
2¾	2	89	80	93	87	99	99	139	136	103	104
1¾	3	94	89	94	91	101	100	133	136	105	107
0	5	94	95	98	95	100	102	129	138	103	105

Acid medium: 4% *aqua regia*.
Concentration of noble metals, *ppm*:
Solutions (*a*) Pt, 100; Rh, 10; Pd, 10; Ru, 50; Au, 10.
(*b*) Pt, 200; Rh, 20; Pd, 20; Ru, 100; Au, 20.
Figures not correct for any changes due to change in nebulizer efficiency as composition is altered.

air–acetylene flame for the propane–butane–air flame used when copper[1] was added. Since the effects of these releasing agents on mutual interference had not been reported for all the noble metals, the present tests were related to all the noble metals that had sufficient sensitivity to enable them to be measured. The results of these tests are presented in Table V, together with absorption data from which the relative sensitivities in the various media can be estimated.

Lanthanum and uranium were the most effective releasing agents for the removal of mutual interferences of all the noble metals. A poor recovery for rhodium (55%) was obtained when copper plus cadmium was tested, and although a full recovery was

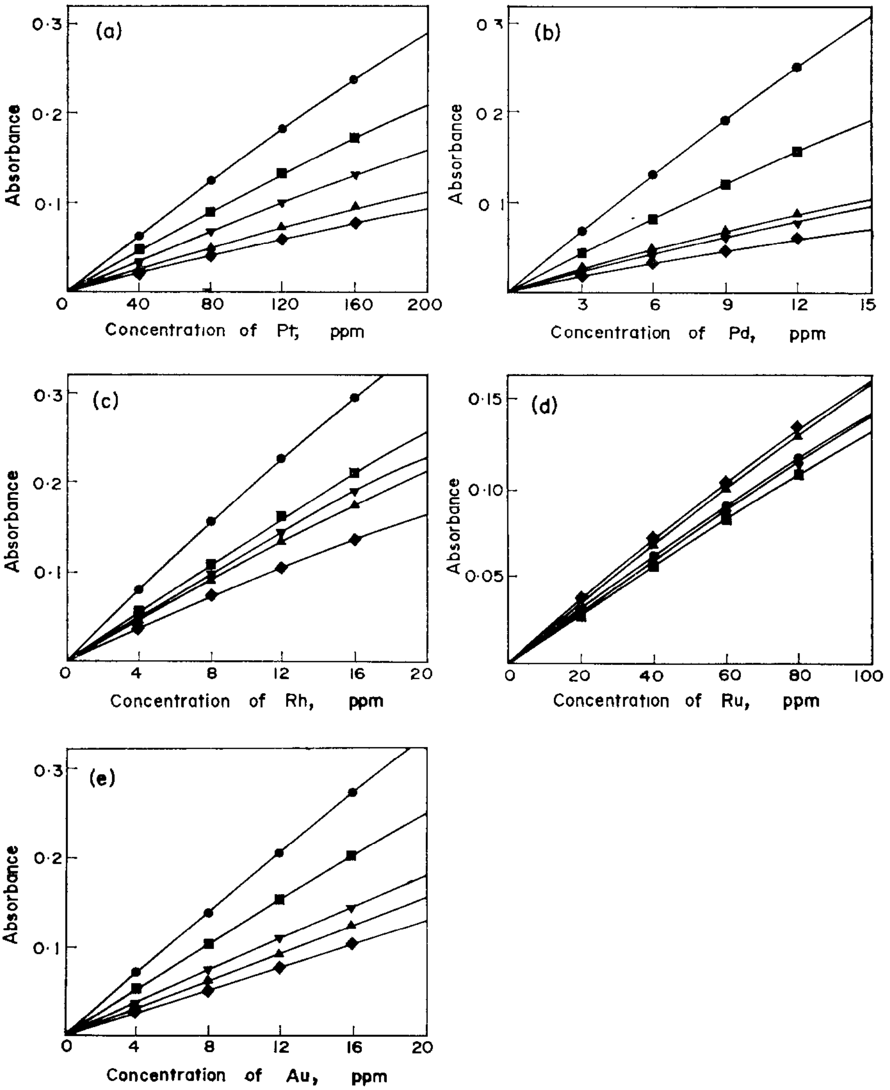


FIG. 2.—The effect on sensitivity, of varying the ratio of nitrous oxide to air, with acetylene as fuel gas.

	Air, l./min	N_2O, l./min
●	5	0
■	3½	1
▼	2¾	2
▲	1¾	3
◆	0	5

obtained by the use of copper sulphate the sensitivity for rhodium was significantly lowered. Palladium in this medium (copper sulphate) was subject to interference (110% recovery) and the sensitivity was lowered. Of the two releasing agents, lanthanum and uranium, the latter was preferred because of its slight superiority in removing mutual interference effects and because it offered the greater improvement in sensitivity.

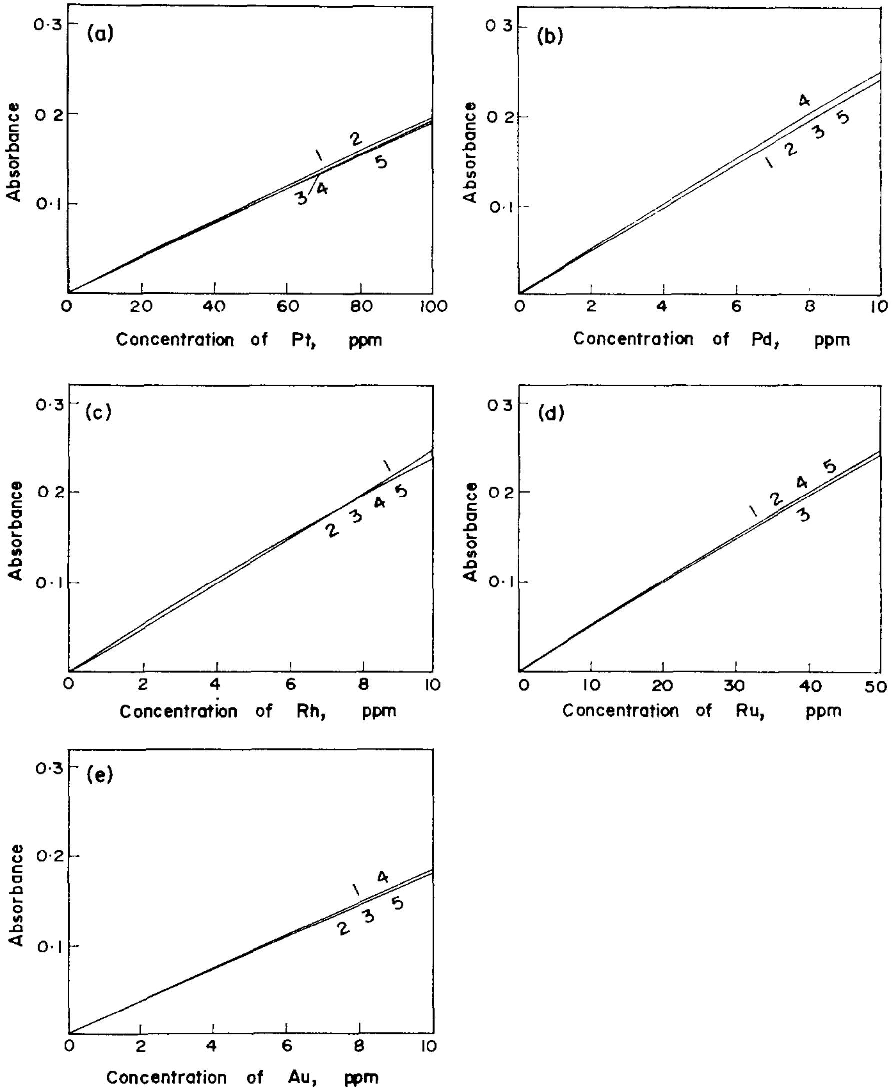


FIG. 3.—The effect of varying amounts of uranium on the calibration curves of the noble metals in a 4% *aqua regia* medium.

1. 5 g/l. of uranium.
2. 10 g/l. of uranium
3. 20 g/l. of uranium.
4. 30 g/l. of uranium.
5. 30 g/l. of uranium.

Uranium as a releasing agent in various acid media.* Because the calibration curves obtained for the noble metals in 4% v/v *aqua regia* in the presence of 0·5–4% w/v uranium were virtually identical and essentially linear, and it had been shown that 1% w/v of U removed mutual interference effects, it was concluded that the addition of uranium was not critical over this range, and decided to use 1% w/v of uranium for all subsequent investigations.

* The uranium was added as a solution (250 mg of U per ml) of U_3O_8 in 10% *aqua regia* solution

TABLE V.—THE VARIATION OF ABSORBANCE OF THE NOBLE METALS AND MUTUAL INTERFERENCES WHEN VARIOUS RELEASING AGENTS ARE ADDED

Noble metal	La		Cu/Cd		$CuSO_4$		U	
	Rec. %	Abs.*	Rec. %	Abs.*	Rec. %	Ads.*	Rec.* %	Abs.*
Pt	102	0·228	101	0·232	102	0·223	102	0·264
Pd	101	0·241	105	0·255	110	0·140	100	0·256
Rh	97	0·141	55	0·059	100	0·078	101	0·212
Ru	98	0·226	99	0·238	100	0·234	100	0·248
Au	97	0·164	103	0·175	100	0·150	101	0·185

La—1% lanthanum, 50% v/v hydrochloric acid medium.

Cu/Cd—0·5% copper and 0·5% cadmium (added as the sulphates), 10% v/v hydrochloric medium.

$CuSO_4$—2% copper (added as sulphate) 10% v/v hydrochloric acid medium.

U—1% U (added as a solution derived from U_3O_8) 4% *aqua regia* medium.

All solutions contain, *ppm*, Pt, 100 Pd, Rh and Au 10 each; Ru, 50.

* = Absorbance of the noble metal in the solution containing all the metals together. No scale expansion was used.

Tests on solutions containing the noble metals and uranium, with variation of the amounts of hydrochloric and nitric acids while maintaining the total acid concentration at 4% v/v, indicated that it was not necessary to remove nitric acid (Table VI).

High acid concentrations are necessary when an analysis is made of cupellation prills to which silver has been added, in order to maintain the silver in solution. Recovery tests (Table VII) on solutions of noble metals in 40% v/v hydrochloric acid–1% v/v nitric acid medium in the presence of 50 ppm of silver and 1% w/v of uranium,

TABLE VI.—THE VARIATION OF ABSORBANCE OF EACH OF THE NOBLE METALS WITH VARYING ACID COMPOSITION IN THE PRESENCE OF URANIUM AND THE OTHER NOBLE METALS

Acid ratio	Absorbance				
$HCl:HNO_3$	Pt	Pd	Rh	Ru	Au
4:0	0·080	0·10	0·094	0·032	0·071
3:1	0·081	0·10	0·096	0·032	0·072
2:2	0·083	0·10	0·096	0·032	0·072
1:3	0·081	0·10	0·094	0·032	0·072
0:4	0·084	0·10	0·097	0·032	0·071

Total acid concentration maintained at 4% v/v.

Noble metal concentration in each solution (*ppm*); Pt, 20; Pd, 2; Rh, 1·8; Ru 4; Au, 2·4

TABLE VII.—RECOVERY OF NOBLE METALS IN HIGH ACID CONCENTRATION (40% v/v HYDROCHOLORIC ACID + 1% v/v NITRIC ACID) IN THE PRESENCE OF 50 p.p.m OF SILVER AND 1% w/v URANIUM, *ppm*

Solution	Pt		Pd		Rh		Ru		Au	
	add.	rec.	add.	rec.	add.	rec.	add.	rec.	add.	rec.
1	40	40·5	12	12·1	12	11·8	60	60·0	12	12·2
2	120	120	12	12·2	4	3·96	60	59·4	12	12·1
3	120	120	4	4·12	12	12·0	60	59·4	12	12
4	120	120	12	12·2	12	11·8	60	60	4	4·16
5	120	118·5	12	12·0	12	12	20	20	12	11·9

showed that the uranium still removed the mutual interference effects and that this amount of silver could be tolerated.

Precision and accuracy of the uranium-addition method. Reproducibility tests carried out on 20 solutions of the noble metals in a 20% v/v hydrochloric acid + 1% v/v nitric acid medium containing 1% w/v of uranium, yielded coefficients of variation of 0·6, 0·5, 0·3, 5·0, 1·0, 1·3 and 1·3% respectively for platinum, palladium, rhodium, ruthenium, gold, silver and lead. The solutions tested contained the noble metals, silver and lead in the concentrations (ppm) associated with a solution of a typical cupellation prill, *viz.* Pt 80; Pd 45; Rh 10; Ru 1·5; Au 2·5; Ag 30; Pb 20. The high coefficient of variation for ruthenium was a function of the low concentration determined. As there was no reason to believe that the precision would be adversely affected by the use of a 40% v/v hydrochloric acid medium, no precision tests were carried out on this medium.

Because standard samples were not available, the accuracy of the method with uranium as a releasing agent was estimated by comparison of the results obtained by AAS with those obtained by chromatographic, chemical and spectrographic analyses (Table VIII). The ruthenium level of these samples, after suitable dilution for the

TABLE VIII.—A COMPARISON OF RESULTS OBTAINED BY ATOMIC-ABSORPTION SPECTROSCOPY WITH URANIUM AS A RELEASING AGENT, WITH THOSE OBTAINED BY OTHER TECHNIQUES

Sample description	Method of analysis	Results obtained, *ppm* in original sample				
		Pt	Pd	Rh	Ru	Au
S2	AAS	4·89	0·70	0·24		0·32
		4·80	0·69	0·23		0·33
	Chromatographic*[6]	4·99	0·60			
S1	AAS	4·93	0·87	0·26		0·22
		5·14	0·88	0·26		0·23
	Spectrographic[7]	5·14	0·89	0·29	0·02	0·19
		5·03	0·91	0·28	0·03	0·18
		5·09	0·94	0·30	0·03	0·21
	Chemical[8]	4·88	0·88	0·32		0·22
		4·96	0·78	0·29		0·17
Chromite	AAS	3·09	1·02	0·42		0·04
		2·93	1·02	0·40		0·03
	Spectrographic	3·29	1·04	0·49	<0·07	0·04
		3·18	1·06	0·47	<0·07	0·04
	Chromatographic	3·04		0·38		
		2·92		0·35		
Concentrate	AAS	4701	119	12		113
		4680	118	11		115
		4686	116	12		116
	Spectrographic	4740	124	12	39	116
		4710	117	12	49	135
		4776	121	11	30	134
	Chromatographic	4637	126			
		4634	117			
		4750	131			
	Chemical		138			129
			136			134
			132			141

* Average of 14 measurements.

measurement of the other noble metals, was too low to be measured by AAS. The agreement between the various techniques was acceptable, and it is considered that the accuracy of the atomic-absorption technique, with uranium being used as a releasing agent for the removal of mutual interference effects, is at least as good as that of the other techniques.

Base-metal interferences in the presence of uranium

Although reliable results for the determination of the noble metals in solutions of prills were obtained, with uranium as a releasing agent, the presence of relatively large amounts of some base metals resulted in significant interferences, which were not removed by the uranium. The effects of those base metals likely to be encountered

Table IX.—Base metal, gold and silver interferences in 4% *aqua regia* medium

Interfering metal	Concn. level tested, *ppm*	Recovery, %				
		Pt	Pd	Rh	Ru	Au
Pb,Cr,Al	100, 500					
Se, Cd.				97–103 for all		
Au, Ni, Te	100			97–103 for all		
Na	500			97–103 for all		
Ag	100†	100	103	94	97	98
Pb	5000†	100	100	94	95	95
Sn	100	102	100	99	96	98
	500	98	99	96	95	97
	5000	96	93	79	95	98
Mg	100	99	100	95	98	98
	500	97	99	94	96	97
	5000	94	94	91	95	94
Cr	5000	93	97	77	87	98
Co	100	96	96	95	97	98
	500	96	96	93	98	95
	5000	93	100	72	99	97
Fe	100	96	96	96	98	95
	500	96	96	94	98	97
	5000	93	96	91	95	102
Ni	500	93	94	87	95	95
	5000	90	95	46	96	95
Al	5000	93	96	91	99	98
Se	5000	98	96	95	100	98
Te	500	96	96	97	99	95
	5000†	97	96	98	76	98
Ca	100	97	96	98	99	97
	500	94	96	91	100	97
	5000	93	97	91	99	98
Cu	100	96	98	98	99	98
	500	96	95	94	99	97
	5000	93	95	71	96	98
Na	100	96	97	97	99	97
	5000	94	97	95	99	97
Cd	5000	96	97	97	100	98
S*	100	96	94	98	99	94
	500	96	95	97	99	94
	5000	81	86	57	87	88

Noble-metal concentrations, *ppm*, Pt, 100; Pd, Rh and Au, 10; Ru, 50. Uranium 1% w/v.

* Added as SO_4^{2-}.

† Precipitation.

were tested in 4% v/v *aqua regia* and 10% v/v hydrochloric acid media and are shown in Tables IX and X. Errors of less than ±3% were interpreted as not constituting a definite interference. Interference effects were usually more evident in the 4% *aqua regia* than in the 10% hydrochloric acid medium. It was observed that rhodium was particularly prone to serious interference (>10% error). Large amounts of copper and nickel resulted in poor recoveries for rhodium in both media, whereas cobalt and chromium affected rhodium to a greater extent in 4% *aqua regia* than in 10% hydrochloric acid. The effect of sulphate was marked in both media; the absorption of all the noble metals, with the exception of palladium in 10% hydrochloric acid, was seriously suppressed by sulphate equivalent to 5000 ppm of S. Where precipiation occurred, as with silver, lead and tellurium, losses of noble metals were attributed to occlusion in the precipitates. Many of the interferences listed were not serious (<5% error) and usually occurred at the highest levels of interferent concentration tested (5000 ppm).

The use of vanadium as a releasing agent in perchloric acid medium. Because several of the base metals that caused serious interference effects (*e.g.*, Cu, Ni, Cr) would be present in some materials requiring analysis, it was decided to investigate the use of a releasing agent other than uranium. It was found that a 1% w/v solution of vanadium in 20% v/v perchloric acid medium removed mutual interference effects (Fig. 1) and considerably improved the recoveries of the noble metals in the presence of relatively large amounts (5000 ppm) of base metals. The metals tested were those

TABLE X.—BASE-METAL, GOLD AND SILVER INTERFERENCES IN 10% V/V HYDROCHLORIC ACID MEDIUM

Interfering metal	Concn. level tested, *ppm*	Recovery, %				
		Pt	Pd	Rh	Ru	Au
Se, Cd	100, 500,			97–103 for all		
	5000			97–103 for all		
Pb,Sn,Co						
Fe,Ni,Al	100, 500			97–103 for all		
Te,Ca,Cu,S						
Au,Cr,Mg	100			97–103 for all		
Ag	100†	100	99	94	99	100
Pb	5000†	98	98	78	97	97
Sn	5000	94	98	98	97	111
Mg	500	96	99	99	98	97
	5000	92	98	94	94	96
Cr	500	96	101	101	100	100
	5000	92	96	93	91	96
Co	5000	96	99	96	97	99
Fe	5000	95	99	94	97	101
Te	5000	96	99	98	100	99
Ni	5000	97	100	89	100	101
Ca	5000	95	103	98	98	101
Al	5000	95	97	94	93	95
Cu	5000	94	96	89	98	97
Na	100	102	106	102	103	101
	500	105	108	105	106	106
	5000	100	106	101	104	105
S*	5000	83	99	66	86	95

Noble metal concentrations, *ppm*, Pt, 100; Pd, Rh, and Au, 10; Ru, 50. Uranium 1% w/v.
† Precipitation.
* Added as SO_4^{2-}.

described in the previous section. The presence of 100 ppm of silver and 5000 ppm of lead resulted in significant losses of rhodium owing to occlusion in the chloride precipitates, and in replicate tests it was found that, on occasions, the presence of iron and tin caused a serious loss of gold, probably owing to reduction to the metal in the evaporation steps required for the removal of excess of nitric acid (to be discussed later). The presence of 5000 ppm of Mg, Cr, Co, Ni, Al, Se, Te, Cu, Na, or Ca and 100 ppm of Au usually resulted in errors of less than 5 %. Sulphate usually suppressed the absorption of rhodium to a larger extent than that of the other noble metals, (*e.g.*, 85 % recovery for rhodium in the presence of 1500 ppm S). However, up to 200 ppm of S had no effect on the absorption of any of the noble metals.

As mentioned earlier, unknown amounts of hydrochloric and nitric acids were undesirable when the vanadium–perchloric acid method was being used. This is shown in Table XI where the effect of various amounts of nitric acid, hydrochloric acid, and *aqua regia* is shown. Because, in this test, unknown amounts of these acids were first removed by fuming in perchloric acid, ruthenium was lost as RuO_4 and could not be measured. The addition of controlled amounts of the acids indicated that a certain amount of variability in the absorption measurements of gold and particularly of palladium could result if the concentration of the acids were not controlled.

In this method a solution of $VOCl_2$ in hydrochloric acid is added in definite amounts after removal, by evaporation, of any unknown amounts of hydrochloric or nitric acids, in order to control the concentration of hydrochloric acid. Noble metals and gold in particular, can be reduced when evaporated to dryness[9] so lithium chloride (10 mg Li) is added before evaporation on a water-bath and the salts are never baked. (These precautions did not always prevent the reduction of gold when iron or tin was present.)

Precision and accuracy of the vanadium–perchloric acid method. Tests of the precision of the method carried out on 48 solutions of noble metals in the absence of base metals, yielded coefficients of variation of 1·4, 1·4, 1·2, 1·4 and 1·1 % for platinum,

Table XI.—The effect of various acid media and acid concentrations on the determination of the noble metals in the presence of vanadium (1 % w/v) and perchloric acid (20 % v/v)

Acid present, %		Recovery %				
	% v/v	Pt	Pd	Ru	Ru*	Au
HNO_3	2·5	100	102	99	—	99
	5	100	100	99	—	100
	7·5	98	100	97	—	99
HCl	2·5	100	104	100	—	101
	5	100	106	100	—	104
	7·5	99	106	100	—	104
Aqua regia†	2·5	100	111	100	—	106
	5	102	115	100	—	107
	7·5	102	122	100	—	108

Noble metal concentrations, *ppm*
Pt, 40; Pd, 4; Rh, 3·2 ; Ru, 24.:
Au, 4·8.

* Ru not measured owing to loss of RuO_4 during treatment; see text.

† Added as a solution of 3:1 v/v *aqua regia*.

palladium, rhodium, ruthenium and gold, respectively, at concentration levels 65, 6·4, 4·8, 25 and 8 ppm respectively.

Because standard samples were not available, true accuracy tests could not be carried out. However, a comparison of results obtained when the vanadium–perchloric acid method and the method with uranium in 4% *aqua regia* were applied to portions of two bulk solutions obtained by the dissolution of prills, the vanadium–perchloric acid method gave satisfactory results, as indicated in Table XII.

TABLE XII.—COMPARATIVE ANALYSIS OF NOBLE-METAL SOLUTIONS* WHEN URANIUM AND VANADIUM ARE USED AS RELEASING AGENTS

Solution	Sample, *ml*	Noble-metal concentrations found, *ppm*									
		Pt		Pd		Rh		Ru†		Au	
		U	V	U	V	U	V	U	V	U	V
TR	2	149	144	27·3	27·9	35·4	35·4	71	73	32·3	35·0
	3	150	146	27·4	27·7	34·8	35·0	77	77	32·6	34·3
	4	149	143	27·0	28·1	35·7	35·6	78	79	33·2	34·4
	5	149	143	27·0	27·6	35·5	35·3	80	80	33·8	34·1
TP	2	368	363	16·9	19·5	11·9	10·0	224	229	63·8	66·3
	3	366	358	19·2	19·1	11·6	10·6	228	225	64·7	67·1
	4	366	363	19·0	19·0	11·3	10·9	231	231	64·4	66·4
	5	365	360	18·9	19·1	11·4	11·1	229	229	64·0	65·7

* These solutions were prepared from cupellation prills.

† Includes added ruthenium to give a measurable concentration.

DISCUSSION

It was confirmed that in the atomic-absorption measurement of the noble metals interferences from the noble metals themselves and from a number of base metals were serious.

The use of the nitrous oxide–acetylene flame as a means of reducing mutual interferences successfully eliminated such effects in the determination of rhodium, as found by Atwell and Hebert.[5] Interferences were also eliminated for platinum, and palladium and gold could be determined as effectively as with the air–acetylene flame. The nitrous oxide flame was not effective in the elimination of interferences in the determination of ruthenium and this, coupled with the overall reduction in sensitivity occurring with this flame, ruled out this approach as a simple means of determination of all the noble metals in one solution.

The observations on the use of various additives as releasing agents for the removal of mutual interferences confirm the published data. In general the additives have been found to be effective for more noble metals than were originally examined but only lanthanum and uranium were found to be effective for all of them. The observations on additives were at variance with the published data in only one instance—contrary to Strasheim and Wessels[1] it was found that the addition of copper sulphate removed the mutual interferences with rhodium. This difference can be attributed to the use of the hotter (air–acetylene) flame.

Base metal interferences, have previously been overcome by the addition of a mixture of copper and cadmium sulphate[4] or by the use of a nitrous oxide flame.[5] These methods were, however, shown to be inadequate in the removal of the mutual interferences associated with the determination of *all* the noble metals examined. The addition of vanadyl chloride as a releasing agent effectively eliminated both mutual and base metal effects even when the base metal concentration was appreciable. The relative merits of the uranium and vanadium methods are worth consideration. The uranium method is simple, requiring only that the sample be dissolved, uranium added and appropriate dilutions made. Acid and uranium concentrations are not critical. Up to 0·5 mg of silver can be maintained in solution by the use of a 40% v/v hydrochloric acid medium. Small amounts of base metals such as lead (20–50 ppm) cause no interference but the method is not applicable to solutions containing significant amounts of base metals.

The vanadium method, although eliminating both mutual and base-metal interferences, requires stricter control of the acid content of the final solution and care must be taken, when removing free nitric acid, to avoid a loss of gold by reduction, especially in the presence of iron and occasionally tin. Lead and silver interfere by occlusion of the noble metals in the precipitated chlorides, the degree of occlusion varying with the conditions of precipitation.

It has been shown by Beyerman[9] that appreciable losses of gold can occur if chloride solutions of this metal are evaporated to dryness. Thus, in the removal of free nitric acid the evaporation should be only to incipient dryness. If losses by reduction are to be avoided, especially in the presence of iron, either the presence of nitric acid should be avoided or the iron be removed before the evaporation step. The loss of gold and the other noble metals would be accelerated if easily reducible metals such as tellurium and selenium were present and the evaporation were taken too far.

Large amounts of lead and silver would need to be removed before measurement. Fortunately, silver and lead are normally only present in significant amounts in cupellation prills from the lead collection procedure, and such prills would be analysed by the uranium-addition technique.

It is apparent, therefore, that the uranium and vanadium methods are useful for different collection methods. Cupellation prills obtained from the lead collection procedure are relatively free from base metals and can best be analysed by the uranium-addition method. Solutions of the noble metals collected by the nickel sulphide procedure, or those obtained by acid extraction of the ores containing significant amounts of base metals, can best be analysed by the vanadium-addition method. Solutions freed from base metals by ion-exchange techniques could be analysed by the uranium-addition method.

The two approaches are therefore capable of being applied to the analysis of the noble metals collected from ores by a variety of procedures provided that the concentrations of the noble metals and any base metals in the solution used in the final analysis can be adjusted to suitable concentration levels.

Acknowledgement—The authors wish to thank the Director of the National Institute for Metallurgy for permission to publish this paper.

Zusammenfassung—Eine Anzahl ernsthafter Störungen bei der Bestimmung der Edelmetalle durch Atomabsorptions-Spektrophotometrie wurden untersucht und Wege erörtert, um sie zu beseitigen. Die Verwendung einer Distickstoffoxid-Acetylen-Flamme verminderte viele Störungen, aber auch die Empfindlichkeit. Zugaben von Lanthan, Kupfersulfat, Kupfer + Cadmiumsulfat, Uran und Vanadium als Mittel zur Freisetzung der Edelmetalle waren bei der Beseitigung von Störungen für ein oder mehrere Edelmetalle in der Luft-Acetylen-Flamme wirksam. Zugaben von Uran erwiesen sich als wirksam beim Beseitigen gegenseitiger Störungen der Edelmetalle (Osmium und

Iridium wurden nicht geprüft), wogegen Vanadium gegenseitige Störungen und solche durch unedle Metalle beseitigte. Genauigkeit und Richtigkeit der Analysenmethoden mit Uran und Vanadium waren annehmbar; die Anwendung dieser Methoden auf die Analyse edler Metalle, die mit verschiedenen Verfahren angereichert wurden, wird kurz diskutiert.

Résumé—On a étudié un certain nombre d'interferences sérieuses dans la détermination des métaux nobles par spectrophotométrie d'absorption atomique, et l'on a envisagé des voies pour les éliminer. L'emploi de la flamme protoxyde d'azote-acetylène réduit nombre de ces interferences, mais réduit aussi la sensibilité. Des additions de lanthane, sulfate de cuiver, cuivre + sulfate de cadmium, uranium et vanadium comme agents d'élimination sont efficaces pour éliminer les interférence pour un ou plusieurs des métaux nobles dans la flamme air-acétylène. On a trouvé que des additions d'uranium sont efficaces pour l'élimination d'interférences mutuelles associées aux métaux nobles (l'osmium et l'iridium n'ont pas été essayés), tandis que le vanadium élimine les interférences mutuelles et les interférences base-métal. La fidélité et la précision des méthodes d'analyse basées sur l'emploi d'uranium et de vanadium sont acceptables, et l'on discute brièvement de l'application de ces méthodes à l'analyse de métaux nobles recueillis par diverses techniques.

REFERENCES

1. A. Strasheim and G. J. Wessels, *Appl. Spectry*, 1963, **17**, 65.
2. J. C. van Loon, *Z. Anal. Chem.*, 1969, **246**, 122.
3. M. M. Schnepfe and F. S. Grimaldi, *Talanta*, 1969, **16**, 591.
4. J. M. Scarborough, *Anal. Chem.*, 1969, **41**, 250.
5. M. G. Atwell and J. Y. Hebert, *Appl. Spectry*, 1969, **23**, 480.
6. C. Pohlandt and T. W. Steele, *Natl. Inst. Metallurgy, Johannesburg Rept.* 1003, 17th July, 1970.
7. K. Dixon, and T. W. Steele, *ibid.*, to be published.
8. E. W. Fowler, *ibid.*, 971, 5th June 1970.
9. K. Beyermann *Z. Anal. Chem.*, 1964, **200**, 183.

Talanta, 1972, Vol. 19, pp. 197 to 202. Pergamon Press. Printed in Northern Ireland

RAPID SEPARATION AND DETERMINATION OF MERCURY*

IVAN KRESSIN
University of California, Los Alamos Scientific Laboratory
Los Alamos, New Mexico 87544, U.S.A.

(*Received* 4 *March* 1971. *Accepted* 12 *June* 1971)

Summary—An analytical procedure is described for the separation of mercury(II) by extraction into n-octanol from sulphuric acid solution and then back-extraction as the tetraiodo complex. The mercury is determined by measuring the absorbance of this complex at 322 nm (molar absorptivity $1{\cdot}95 \times 10^3$ l.mole^{-1}.cm^{-1}). The procedure is applicable to samples containing copper; the effects of a wide variety of other impurities are tabulated.

MANY ANALYTICAL METHODS have been reported for the determination of mercury. Neutron-activation analysis and spark-source mass spectrometry provide sensitive methods for the detection of mercury but also require expensive equipment and highly trained analysts.[1,2] Atomic-absorption spectrophotometry is commonly used in many modern laboratories.[3] Methods based on extraction with dithizone have probably received the greatest attention, but other reagents have also been reported.[4] Waterbury, for example, has reported the extraction of the mercury–diethyldithiocarbamate complex into carbon tetrachloride.[5] Rogers[6] suggested the use of iodide for the determination of mercury and Kressin and Coleman reported on the spectrophotometric determination of mercury as the tetraiodo complex.[7]

Mercury has an unusually great affinity for the iodide ion and the formation constants of the iodide complexes of mercury(II) (Table I) have been known for many years.[8] Although the formation constants are well known, it is less widely known that tetraiodomercurate(II) absorbs strongly in the near ultraviolet. The present paper reports the conditions required for the use of mercuric iodide complexes for an unusually simple and straightforward separation followed by a specific photometric determination of mercury. The method is based on the extraction of iodide–mercury(II) species into octanol from an acidic solution and back-extraction of the mercury as the tetraiodo complex which is then determined spectrophotometrically.

TABLE I.—FORMATION CONSTANTS OF Hg–I COMPLEXES*

$Hg^{2+} + I^- \rightleftharpoons HgI^+$	$\log K_1 = 12{\cdot}9$
$HgI^+ + I^- \rightleftharpoons HgI_2$	$\log K_2 = 10{\cdot}9$
$HgI_2 + I^- \rightleftharpoons HgI_3^-$	$\log K_3 = 3{\cdot}8$
$HgI_3^- + I^- \rightleftharpoons HgI_4^{2-}$	$\log K_4 = 2{\cdot}2$
$Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$	$\log \beta_4 = 29{\cdot}8$

* See Ref. 8.

EXPERIMENTAL

Apparatus

A Cary Model 14 spectrophotometer was used for photometric measurements and all absorbances were read directly from the recorder scale. Aliquots of standard mercuric sulphate solutions were

---

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

taken with a calibrated pipette. Other volumetric glassware was not calibrated. Extractions were performed in 60-ml separatory funnels, electric motors fitted with a glass stirring rod being used to mix the solutions.

Reagents

Mercuric oxide was used as the primary standard for the determination of molar absorptivities and for calibration curves. The mercuric oxide was dried in a vacuum desiccator before weighing and then dissolved in sulphuric acid. The standard mercuric solution was $0{\cdot}1M$ with respect to sulphuric acid. All reagents used in the preparation of solutions were of analytical grade.

Potassium iodide ($3M$) was found to be quite stable in 10% aqueous ammonia solution, and was used for the back-extraction. The solution was filtered before use, to avoid light-scattering by flocculent impurities.

The $0{\cdot}1M$ potassium iodide and $0{\cdot}1M$ sodium thiosulphate were prepared by dissolving the respective salts in water and used without further treatment.

The n-octanol, Eastman P-871, was used without further purification.

The $9M$ sulphuric acid was prepared by slowly diluting concentrated sulphuric acid with an equal volume of water.

Procedure

Transfer an aliquot of the sample solution containing 1–200 μg of mercury(II) to a separatory-funnel and add an equal volume of $9M$ sulphuric acid. Stir the mixture and add 0·5 ml of $0{\cdot}1M$ potassium iodide and 10 ml of n-octanol. Stir the mixture for one minute and discard the aqueous phase. Wash the alcohol phase twice with 3-ml portions of water to remove the excess of sulphuric acid, and discard the wash solution. Back-extract the mercury with three 3-ml portions of $3M$ potassium iodide, and collect the extracts in a volumetric flask (10-ml if the mercury content is expected to be in the 1–40 μg range, otherwise 25-ml). Add to the flask 0·5 ml of $0{\cdot}1M$ sodium thiosulphate and dilute to volume with water. Measure the absorbance of the mercuric tetraiodo complex at 322 nm against air in the reference beam. Correct for the absorbance of the reagents by performing the extraction on a volume of water equal to that of the sample.

DISCUSSION AND RESULTS

In the presence of iodide, mercury(II) is extracted rapidly from sulphuric acid solution into n-octanol, but as the tetraiodo complex is not extracted quantitatively a large excess of iodide should be avoided during the first extraction of the mercury. It is considered that the tri-iodo complex of mercury(II) is the mercury complex extracted, because increasing concentrations of iodide lowered the fraction of mercury extracted by the *n*-octanol. If this is the case, the complex is presumably protonated to give a neutral species. From the analytical point of view it is immaterial which species is extracted provided extraction is complete. The amount of iodide added before extraction of mercury may vary within ±50% of that recommended, without causing loss of mercury. The mercury(II) is quantitatively extracted into octanol from $>2M$ sulphuric acid but the convenience of adding a volume of $9M$ sulphuric acid equal to that of the sample aliquot justified using the larger volume of acid. Approximately 98% of the mercury is extracted from $1{\cdot}0M$ sulphuric acid. The mercury is not back-extracted by the water wash but the excess of sulphuric acid should be removed, otherwise the ammonium sulphate produced will inhibit phase separation during the back-extraction step. The water wash also removes any other ions which might interfere if present in the final solution. More than three washes with water may be required if copper or nitrate is present in the sample. After the water wash, mercury is back-extracted into $3M$ potassium iodide, three successive extractions being used for quantitative recovery. Iodide in acid solution is readily oxidized by air, therefore the tri-iodide ion (I_3^-) formed during the extraction is reduced by the addition of thiosulphate before the absorbance measurements are made.

Iodo-mercuric complexes, iodide and tri-iodide (I_3^-) all absorb strongly in the ultraviolet region. Mercuric iodide, Fig. 1A, has two absorbance maxima. The absorbance peak at 264 nm has a molar absorptivity of approximately 560 l.mole^{-1}.mm^{-1} and the sharp one at 210 nm an absorptivity of approximately 2·86 × 10^4 l.mole^{-1}.mm^{-1}. There are several reasons why the absorption by mercuric iodide at 210 nm is unsuitable for the spectrophotometric determination of mercury; from the formation constants it is apparent that its concentration will depend on the free iodide concentration, and the iodide itself absorbs strongly below 270 nm. The use of the absorption due to the mercuric tri-iodo complex was rejected for similar reasons.

The absorption spectrum of mercuric tetraiodo complex is shown in Fig. 1B. The absorption peak at 322 nm has a molar absorptivity of 1·95 × 10^4 l.mole^{-1}.cm^{-1}, and that at 270 nm about 3·50 × 10^4 l.mole^{-1}.cm^{-1}. Since iodide does not absorb

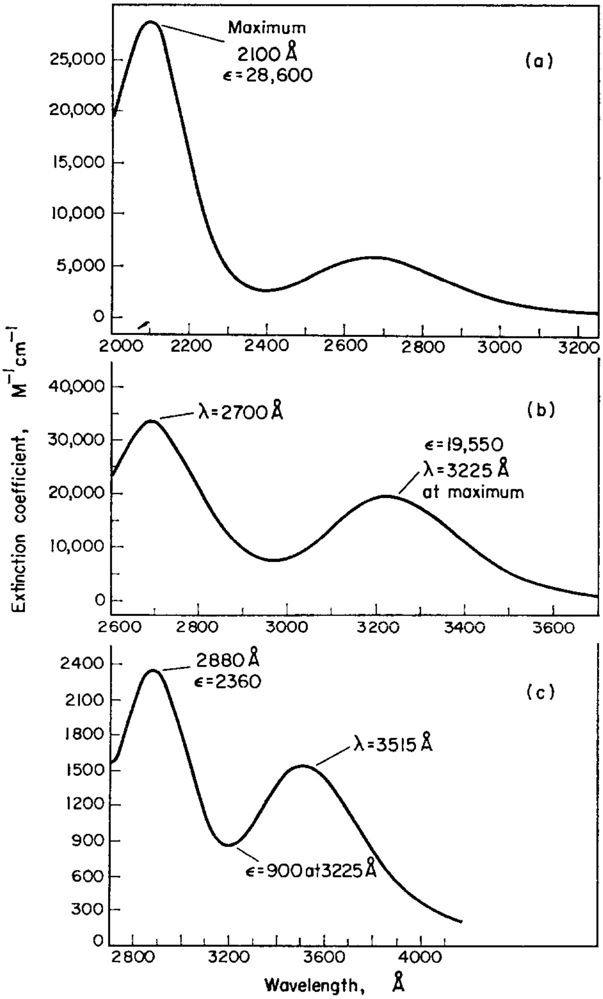


FIG. 1.—Absorption spectrum of (A) HgI$_2$; (B) HgI$_4^{2-}$ in 1*M* potassium iodide; (C) I$_3^-$.

at above 300 nm but does so appreciably below this wavelength, the analytical use of the 270-nm peak would require an accurate knowledge of the iodide concentration. For these reasons, the longer-wavelength peak at 322 nm was chosen.

From the formation constants, it is apparent that moderately high iodide concentrations are needed to drive the reaction, $HgI_3^- + I^- \rightleftharpoons HgI_4^{2-}$ to completion. Figure 2 shows the variation in the absorption spectrum of the mercuric tetraiodo complex with changes in the iodide concentration. The presence of the isosbestic points confirms the presence of just two absorbing species; namely HgI_3^- and HgI_4^{2-} and the results are in good accord with the reported equilibrium constant for this reaction. The use of a final potassium iodide concentration much lower than 0·6*M* clearly leads to a mixture of mercury complexes and should be avoided.

The tri-iodide ion has an absorption peak (Fig. 1C) on either side of 322 nm with a minimum very near this wavelength. A small concentration of this ion could be tolerated but the addition of 0·5 ml of 0·1*M* sodium thiosulphate effectively removes tri-iodide from the solution.

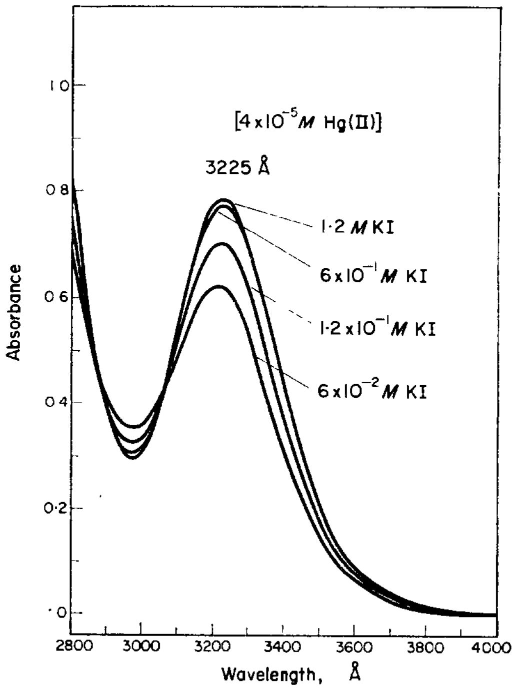


FIG. 2.—Effect of various concentrations of potassium iodide on the absorption spectrum of Hg(II) species in the region of the 322 nm peak of the HgI_4^{2-} complex.

Colour stability

The mercury tetraiodo complex is stable for long periods in 1·0*M* potassium iodide solution. With the addition of sodium thiosulphate to remove tri-iodide the absorbance is stable for more than 24 hr. The effect of varying the pH was investigated and no change was found over the pH range 1–14; however, as potassium iodide solutions are more stable at pH above 7, a higher pH was chosen.

Variations in temperature above 30° and below 20° do have a measurable effect, but no error is introduced if the solutions are maintained at 25° ± 5°.

The precision was checked in two ways. With samples of mercuric oxide weighed directly into volumetric flasks, 34 determinations yielded a molar absorptivity of $1{\cdot}95 \times 10^3$ l.mole^{-1}.cm^{-1} with a relative standard deviation of 0.4%. The final concentration of mercury varied from $1{\cdot}5 \times 10^{-5}$ to $4 \times 10^{-5}M$, corresponding to a net absorbance of 0·3–0·8. Another check on the precision was made by taking 34 aliquots containing from $3{\cdot}1 \times 10^{-7}$ to $8{\cdot}0 \times 10^{-6}$ mole of mercury, following the procedure, and determining the slope of the line by the linear regression method. The slope was 10·36 μg/ml per absorbance unit, with a correlation coefficient of 0·9998 and an intercept of −0·0015 ± 0·0005 at the 95% confidence interval. The data show that Beer's law is obeyed over the concentration range investigated and that mercury can be determined with a high degree of precision.

The recovery of mercury in the extraction procedure was checked in the following manner. Solutions of mercuric sulphate were added directly to 25-ml volumetric flasks and the absorbance due to the mercuric tetraiodo complex was measured. The extraction procedure was performed on equal amounts of mercuric sulphate and the absorbances were measured after the extraction. Within the experimental error, the absorbances of the two sets of solutions showed that the mercury was recovered in this extraction procedure.

Interferences

A detailed investigation of every conceivable type of sample which might contain mercury would be impossible, but a large number of ions were investigated. The ions tested for interference were present at concentrations one thousand times greater than that of the mercury and an ion was not considered as causing an interference unless the results for mercury were changed by more than 2%. The species which do not interfere are: Li, Na, K, Mg, Ca, Sr, Ba, La, Ti(IV), Zr, V(V), Nb, Ta, Cr(III), Mo(VI), W(VI), Fe, Co, Zn, Cd, Ce(III), Al, Sn(IV), As(V), Te, fluoride, chloride, phosphate, acetate and hydrogen peroxide. Those which necessitate some precautions are listed in Table II.

In general, ions that interfere are those that react with potassium iodide and absorb strongly at 322 nm. Strong reducing agents will also interfere. Many of the interfering elements listed in Table III could be tolerated at lower concentrations and would not be expected at such high concentrations in most samples. Cyanide, tin(II) and titanium(III) would interfere at any concentration.

TABLE II.—MASKING OF SOME POSSIBLE INTERFERENCES

Ion	Precaution
Ni(II)	Solution must be saturated with ammonium chloride before the extraction.
Cu(II)	Solution must be saturated with ammonium chloride before the extraction. Solid ammonium chloride must be present during the extraction.
Tl(I)	Solution must be saturated with ammonium chloride before the extraction.
Pb(II)	Solution must be saturated with ammonium chloride before the extraction.
Br^-	Concentrations above 1M interfere.
NO_3^-	This ion absorbs strongly in the ultraviolet, and must be stripped from the octanol by thorough washing before the back-extraction of the mercury.

TABLE III.—IONS THAT AFFECT THE DETERMINATION

$[Ion]/[Hg] = 10^3$	Comment
Ag(I)	Removes iodide and the precipitate interferes with extraction. Small amounts do not interfere.
Bi(III)	Concentrations equal to that of the mercury do not interfere.
Ce(IV)	Extracted; can be reduced with H_2O_2 to eliminate interference.
Mn(II)	Extracted and causes positive errors
Cr(VI)	Extracted; can be reduced with Fe(II)
CN^-	Complexes mercury.
Sn(II)	Reduces mercury.
Ru	Can be removed by fuming with HNO_3.
Pd	Extracted and causes positive errors.
Au	Causes negative errors.
V(III)	Can be oxidized to V(V) to eliminate interference.
Ti(III)	Reduces the mercury.

CONCLUSION

The spectrophotometric determination of mercury as the tetraiodo complex has several advantages to warrant its use. The procedure is applicable to samples containing copper and the method is sensitive, precise, rapid and easy to use. The procedure as described can be performed with chemicals and equipment usually found in a laboratory. Furthermore the method does not suffer from the instability of reagents, as does the dithizone extraction of mercury.

Acknowledgements—The author wishes to acknowledge the support of Dr. E. S. Robinson and Dr. R. Penneman in this study and the helpful suggestions of Dr. J. Coleman.

Zusammenfassung—Ein analytisches Verfahren zur Abtrennung von Quecksilber wird beschrieben. Es wird aus schwefelsaurer Lösung in n-Octanol extrahiert und als Tetrajodokomplex rückextrahiert. Quecksilber wird bestimmt durch Messung der Extinktion dieses Komplexes bei 320 nm (molarer Extinktionskoeffizient $1{,}95 \cdot 10^3$ l mol^{-1} mm^{-1}). Das Verfahren läßt sich auf kupferhaltige Proben anwenden; der Einfluß einer großen Vielfalt anderer Verunreinigungen wird tabellarisch dargestellt.

Résumé—On décrit une technique analytique pour la séparation du mercure(II) par extraction en *n*-octanol à partir d'une solution en acide sulfurique, puis extraction en retour à l'état de complexe tetraiodo. Le mercure est déterminé par mesure de l'absorption du complexe à 320 nm (coefficient d'absorption moléculaire $1{,}95 \times 10^3$ l.mole^{-1}.cm^{-1}). La technique est applicable aux échantillons contenant du cuivre; on présente sous forme de tableau les influences d'une large variété d'autres impuretés.

REFERENCES

1. K. Samsahl, *Anal. Chem.*, 1967, **39**, 1480.
2. S. S. C. Tong, W. H. Gutenman and D. J. Lisk, *ibid.*, 1969, **41**, 1872.
3. W. R. Hatch and W. L. Ott, *ibid.*, 1968, **40**, 2085.
4. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1959.
5. E. A. Hakkila and G. R. Waterbury, *Anal. Chem.*, 1960, **32**, 1340.
6. C. Merritt, Jr., H. M. Hershenson and L. B. Rogers, *ibid.*, 1953, **25**, 572.
7. I. K. Kressin and J. S. Coleman, 22nd Annual Southwest Regional Meeting, ACS, 1967.
8. L. Meites, Editor, *Handbook of Analytical Chemistry*, McGraw-Hill, New York, 1963.

Talanta, 1972, Vol. 19, pp. 203 to 206. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

A voltammetric and chronopotentiometric study of molten alkali acetates

(*Received* 6 *July* 1971. *Accepted* 19 *October* 1971)

MANY papers have been published in recent years regarding molten alkali metal acetates, dealing with characterization of the solvent,[1-3] polarography,[4-6] potentiometry,[7] spectrophotometry[8,9] and conductivity.[10,11] In this communication some preliminary results of a voltammetric and chronopotentiometric study in molten (Na, K) acetates (46·3 mole% sodium acetate) at 250° are reported.

The study deals with the reduction of water and acetic acid, and with the oxidation of hydrogen and hydroxide ions on bright platinum electrodes. Voltammetry was performed with an oscillating platinum microelectrode;[12-14] for chronopotentiometry a vertical platinum foil (61·7 mm^2) was used.

The electrochemically stable range of the solvent is represented by curve *1* in Fig. 1.

All the potentials are referred to an Ag/Ag$^+$(0·1 mole/kg) electrode in (Na, K)NO$_3$ enclosed in a soft glass bulb. This electrode has been used as a reference both in voltammetry and in chronopotentiometry, assuming its potential to be equal to zero.

Curve *1* may be obtained from a melt carefully dried for many hours under high vacuum or a stream of dry nitrogen. A good baseline is obtained only when oxygen is rigorously excluded from the melt, and when certain precautions are taken in pretreating the electrodes.

Normally the last traces of water are difficult to remove and the voltammograms are more like that represented by curve *2*. The wave at about −1·8 V is due to reduction of water according to the reaction

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

as is demonstrated by the composite wave (curve *3*) obtained in a melt with added hydroxide ion and molecular hydrogen.

The height of the anodic wave is limited by the hydrogen pressure; the wave at about −0·8 V is associated with the oxidation of the hydroxide ion and may still be seen after removal of hydrogen gas by passing a stream of nitrogen.

The voltammograms obtained for melts of this kind are not reproducible over prolonged periods, owing to decomposition caused by reaction of the hydroxide ion with the solvent. Some attempts have been made to determine the kinetics of this reaction; it seems to be pseudo-monomolecular with a half-life of about 2 hr, referred to the hydroxide ion concentration.

If glacial acetic acid is added to the melt the shape of the voltammogram becomes that of curve *4*. The hydrogen ion reduction precedes that of water and there is evolution of hydrogen gas at the electrode according to the overall reaction.

$$2H^+ + 2e^- \rightarrow H_2.$$

In the presence of hydrogen gas a composite wave (curve *5*) is obtained.

Oxidation waves of molecular hydrogen, not represented in Fig. 1 for the sake of simplicity, are readily obtained; sometimes these waves show a maximum of the first kind, but this depends on the pretreatment of the electrode.

Chronopotentiometric experiments lead one to the same conclusion regarding the electrochemical behaviour of each species. In Figs. 2 and 3 are represented some typical chronopotentiograms for different solutes. Figure 2 represents a chronopotentiogram obtained in a partially dried melt; the potential break on the reverse branch corresponds to the anodic part of the composite wave of curve *3* (Fig. 1) with the difference that hydrogen gas and hydroxide ions are produced during the forward process.

The shape of the anodic wave remains the same as long as the amount of hydrogen gas produced does not exceed the total solubility in the melt and on the platinum electrode. When this happens gas evolution can be observed at the electrode and hence some hydrogen is lost by a process other than pure diffusion. This event causes the appearance on the anodic wave of a second potential break that corresponds to oxidation of the excess of hydroxide ion formed at the electrode surface.

Curves *a* and *b* in Fig. 3 represent the oxidation of molecular hydrogen and the reduction of hydrogen ion followed by the respective reverse processes.

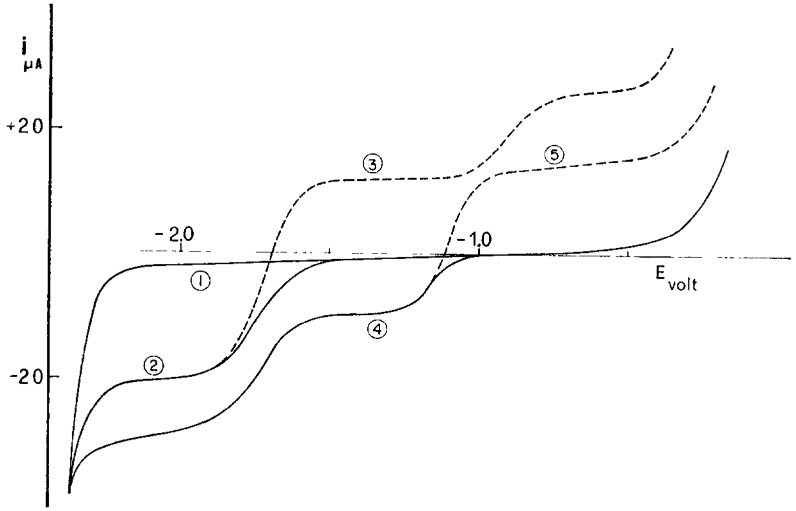


FIG. 1.—Current–potential curves for a platinum microelectrode: (*1*) dry solvent; (*2*) water reduction wave; (*3*) composite wave for the system H_2O/H_2, OH^-; (*4*) hydrogen ion reduction; (*5*) composite wave for the system H_2/H^+.

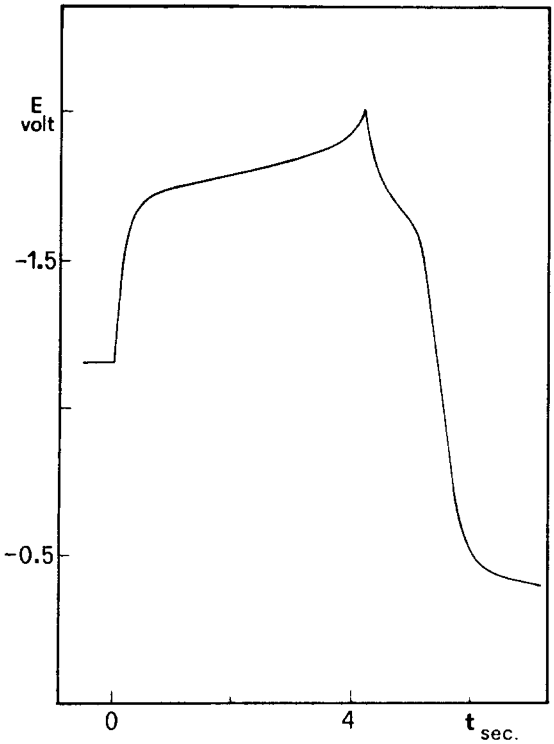


FIG. 2.—Chronopotentiogram with current reversal for water reduction.

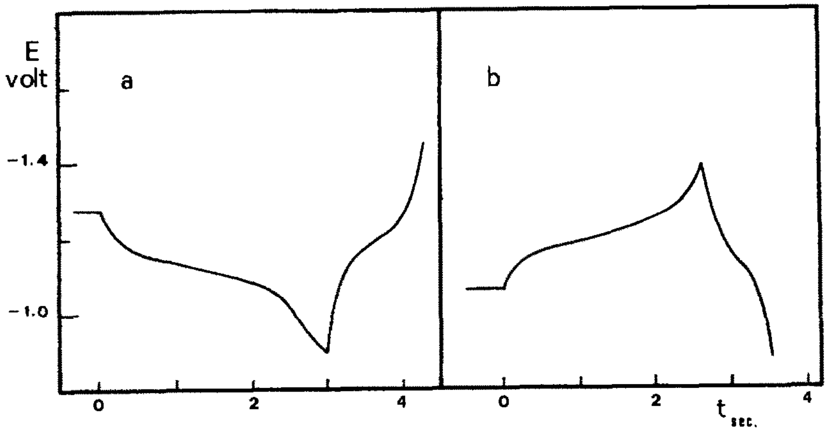


FIG. 3.—Chronopotentiograms with current reversal for: (a) hydrogen oxidation; (b) hydrogen ion reduction.

Both voltammetry and chronopotentiometry have been demonstrated to be suitable methods for the detection of water in acetate melts; this is important because water is the commonest impurity generally found in melts. In addition the reproducibility of the wave-height and of the transition times suggests that these techniques may be used for the determination of each species and hence their solubility. These studies are in progress and will be the subject of a later report.

Acknowledgements—This work was supported by the Italian National Research Council (C.N.R.) The authors wish to thank Prof. Mario Fiorani for helpful discussion and suggestions.

Istituto Chimico dell Universita
degli Studi Camerino
62032 Camerino,
Italy

ROBERTO MARASSI
VITO BARTOCCI
FILIPPO PUCCIARELLI

Summary—The electrochemical behaviour of water, hydrogen ion, and molecular hydrogen has been investigated in (Na,K) acetate melt at 250° with bright platinum electrodes by means of chronopotentiometry and voltammetry.

Zusammenfassung—Die elektrochemischen Verhalten vom Wasser, Wasserstoff Ion und molekularen Wasserstoff werden in einer Schmelze aus (Na,K) Acetat bei 250° durch Voltammetrie und Chronopotentiometrie mit den Platinelektroden untersucht.

Résumé—On a étudié le comportement électrochimique de l'eau, de l'ion hydrogène et de l'hydrogène moléculaire dans la masse fondue d'acétate (Na, K) à 250° avec des électrodes de platine poli au moyen de la chronopotentiométrie et de la voltammétrie.

REFERENCES

1. F. J. Hazlewood, E. Rhodes and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1966, **62**, 3101.
2. R. F. Bartholomew and H. J. Holland, *J. Am. Ceram. Soc.*, 1969, **52**, 402.
3. N. M. Sokolov and E. I. Pochtakova, *Zh. Obschei Khim.*, 1958, **28**, 1348.
4. G. G. Bombi, M. Fiorani and C. Maccà, *Chem. Commun.*, 1966, 455.
5. H. Giess, M. Francini and S. Martini, *Electrochim. Metal.*, 1969, **4**, 17.
6. R. Marassi, V. Bartocci and M. Fiorani, *Chim. Ind.*, 1970, **52**, 365.
7. R. Marassi, V. Bartocci, P. Cescon and M. Fiorani, *J. Electroanal. Chem.*, 1969, **22**, 215.
8. R. A. Bailey, H. Elguindy and J. A. Walden, *Inorg. Chem.*, 1969, **8**, 2526.
9. J. Duffy and M. Ingram, *J. Chem. Soc. A*, 1969, 2398.
10. R. F. Bartholomew, *J. Phys. Chem.*, 1970, **74**, 2507.

11. Z. Halmos, T. Meisel, K. Seybold and L. Erdey, *Talanta*, 1970, **17**, 1191.
12. V. Bartocci, P. Cescon, R. Marassi and M. Fiorani, *Ric. Sci.* 1969, **39**, 585.
13. L. Busulini and P. Cescon, *Ann. Chim.* (*Roma*), 1966, **56**, 852.
14. F. Schiavon, G. A. Mazzocchin and G. G. Bombi, *J. Electroanal. Chem.*, 1971, **29**, 401.

Talanta, 1972, Vol. 19, pp. 206 to 207. Pergamon Press. Printed in Northern Ireland

Statocalcein, a stable Calcein indicator for the EDTA titration of calcium

(*Received* 24 *June* 1971. *Accepted* 15 *September* 1971)

THE COMPOUND $K_2Ca_5Calcein_2$ provides a stable aqueous solution of Calcein which is suitable as an indicator in the EDTA titration of calcium at high pH in the presence of magnesium. Two hundred and ten days after preparation, an aqueous solution of this compound still provided a sharp fluorometric endpoint, in contrast to solutions of Calcein in alkali which decompose within a day or so with the production of material, which gives a disturbing background fluorescence. We propose to call the new material *Statocalcein* (from *stato*, stable or fixed).

The theory of this development is based on the work of Hefley[1] who established the structure of Calcein and worked out the combining ratio and formation constants of the two calcium derivatives. Two ions of calcium combine, stepwise, with Calcein, each being bound by one iminodiacetate group (*i.e.*, both carboxylate groups and the nitrogen atom) and the adjacent phenolic oxygen atoms. The iminodiacetic acid groups and the resorcinol rings are thus tightly packed, minimizing free rotation and presenting a more spherical configuration which is less subject to attack. The idea was to take advantage of this for the preparation of a stock solution, it being immaterial for indicator purposes that the metal being determined is also present in the indicator.

In the union of calcium with Calcein hydrogen ions are displaced. As shown by Hefley, in the titration with alkali of Calcein in the presence of calcium, six hydrogen ions are neutralized per Calcein molecule and a sharp end-point is observed at pH 8. It was proposed simply to isolate from a solution brought essentially to this end-point the compound $K_2Ca_2Calcein$. A solid compound was isolated but it proved to be $K_2Ca_5Calcein_2$.

EXPERIMENTAL

Reagents

Statocalcein; K_2Ca_5*Calcein*$_2$*; dipotassium pentacalcium bis*(3′,6′-*dihydroxy*-4′,5′-*di*[N,N′-*di*(*carboxymethyl*)*aminomethyl*]*fluoran*). Calcein was prepared by the procedure of Hefley[1] starting with metal-free fluorescein obtained by the hydrolysis of diacetylfluorescein. The Calcein was dried in vacuum at 50° for 24 hr. To a slurry of 3·84 g (0·0060 mole) of Calcein in 25 ml of deionized water was added a solution of calcium chloride prepared by dissolving 1·50 g (0·0150 mole) of primary-standard calcium carbonate in hydrochloric acid. With vigorous mechanical stirring, 0·4*M* potassium hydroxide was added dropwise until the pH reached and remained at 8·5. The precipitate formed was filtered off, slurried with 100 ml of demineralized water, and again filtered off. Some of this material was air-dried. The major part was rinsed into a freeze-drying bulb, frozen in liquid nitrogen, and freeze-dried. Both solids were orange. Found: Ca, 13·26%; K, 5·18%; Calcein, 81·0%. Calculated for $K_2Ca_5C_{60}H_{40}O_{26}N_4$: Ca, 13·26%; K, 5·17%; Calcein ($C_{60}H_{40}O_{26}N_4$), 81·57%. (Calcium was determined by EDTA titration following wet ashing with nitric acid plus perchloric acid. Potassium was determined by conversion of Statocalcein into calcium hydroxide plus potassium hydroxide by passage over IRA-400 in the alkaline form, followed by titration with acid and successive and immediate determination of calcium by EDTA titration; potassium was then calculated by difference. Calcein was determined fluorometrically as the dicalcium salt at pH 12, by using a Turner Model 110 fluorometer with appropriate filters, and calibration with pure Calcein as obtained by Hefley.)

Procedure

Stability of indicator solution and evaluation as indicator. For comparison, four solutions were prepared: (1) Calcein, 0·02% in 0·01*M* potassium hydroxide (as recommended in the original paper of Diehl and Ellingboe);[2] (2) Calcein, 0·02% in 1:1 water–ethanol; (3) Statocalcein (air-dried), 0·02% in water; (4) Statocalcein (freeze-dried), 0·02% in water. All solutions were stored in

11. Z. Halmos, T. Meisel, K. Seybold and L. Erdey, *Talanta*, 1970, **17,** 1191.
12. V. Bartocci, P. Cescon, R. Marassi and M. Fiorani, *Ric. Sci.* 1969, **39,** 585.
13. L. Busulini and P. Cescon, *Ann. Chim.* (*Roma*), 1966, **56,** 852.
14. F. Schiavon, G. A. Mazzocchin and G. G. Bombi, *J. Electroanal. Chem.*, 1971, **29,** 401.

Talanta, 1972, Vol. 19, pp. 206 to 207. Pergamon Press. Printed in Northern Ireland

Statocalcein, a stable Calcein indicator for the EDTA titration of calcium

(*Received* 24 *June* 1971. *Accepted* 15 *September* 1971)

THE COMPOUND K$_2$Ca$_5$Calcein$_2$ provides a stable aqueous solution of Calcein which is suitable as an indicator in the EDTA titration of calcium at high pH in the presence of magnesium. Two hundred and ten days after preparation, an aqueous solution of this compound still provided a sharp fluorometric endpoint, in contrast to solutions of Calcein in alkali which decompose within a day or so with the production of material, which gives a disturbing background fluorescence. We propose to call the new material *Statocalcein* (from *stato*, stable or fixed).

The theory of this development is based on the work of Hefley[1] who established the structure of Calcein and worked out the combining ratio and formation constants of the two calcium derivatives. Two ions of calcium combine, stepwise, with Calcein, each being bound by one iminodiacetate group (*i.e.*, both carboxylate groups and the nitrogen atom) and the adjacent phenolic oxygen atoms. The iminodiacetic acid groups and the resorcinol rings are thus tightly packed, minimizing free rotation and presenting a more spherical configuration which is less subject to attack. The idea was to take advantage of this for the preparation of a stock solution, it being immaterial for indicator purposes that the metal being determined is also present in the indicator.

In the union of calcium with Calcein hydrogen ions are displaced. As shown by Hefley, in the titration with alkali of Calcein in the presence of calcium, six hydrogen ions are neutralized per Calcein molecule and a sharp end-point is observed at pH 8. It was proposed simply to isolate from a solution brought essentially to this end-point the compound K$_2$Ca$_2$Calcein. A solid compound was isolated but it proved to be K$_2$Ca$_5$Calcein$_2$.

EXPERIMENTAL

Reagents

Statocalcein; K$_2$Ca$_5$*Calcein*$_2$*; dipotassium pentacalcium bis*(3′,6′*-dihydroxy-*4′,5′*-di*[N,N′*-di*(*carboxymethyl*)*aminomethyl*]*fluoran*). Calcein was prepared by the procedure of Hefley[1] starting with metal-free fluorescein obtained by the hydrolysis of diacetylfluorescein. The Calcein was dried in vacuum at 50° for 24 hr. To a slurry of 3·84 g (0·0060 mole) of Calcein in 25 ml of deionized water was added a solution of calcium chloride prepared by dissolving 1·50 g (0·0150 mole) of primary-standard calcium carbonate in hydrochloric acid. With vigorous mechanical stirring, 0·4*M* potassium hydroxide was added dropwise until the pH reached and remained at 8·5. The precipitate formed was filtered off, slurried with 100 ml of demineralized water, and again filtered off. Some of this material was air-dried. The major part was rinsed into a freeze-drying bulb, frozen in liquid nitrogen, and freeze-dried. Both solids were orange. Found: Ca, 13·26%; K, 5·18%; Calcein, 81·0%. Calculated for $K_2Ca_5C_{60}H_{40}O_{26}N_4$: Ca, 13·26%; K, 5·17%; Calcein ($C_{60}H_{40}O_{26}N_4$), 81·57%. (Calcium was determined by EDTA titration following wet ashing with nitric acid plus perchloric acid. Potassium was determined by conversion of Statocalcein into calcium hydroxide plus potassium hydroxide by passage over IRA-400 in the alkaline form, followed by titration with acid and successive and immediate determination of calcium by EDTA titration; potassium was then calculated by difference. Calcein was determined fluorometrically as the dicalcium salt at pH 12, by using a Turner Model 110 fluorometer with appropriate filters, and calibration with pure Calcein as obtained by Hefley.)

Procedure

Stability of indicator solution and evaluation as indicator. For comparison, four solutions were prepared: (1) Calcein, 0·02% in 0·01*M* potassium hydroxide (as recommended in the original paper of Diehl and Ellingboe);[2] (2) Calcein, 0·02% in 1:1 water–ethanol; (3) Statocalcein (air-dried), 0·02% in water; (4) Statocalcein (freeze-dried), 0·02% in water. All solutions were stored in polyethylene bottles in the dark. The calcium in a stock solution of calcium chloride, 0·02000M, prepared by dissolving 4·0036 g of primary-standard calcium carbonate in hydrochloric acid and diluting to exactly 2 l., was determined periodically by EDTA titration, each of these indicators being used.

A 25·00-ml aliquot of the stock solution of calcium chloride was first treated with about 10 mg of ascorbic acid, 2·5 ml of 5% potassium cyanide solution, 5 ml of 20% triethanolamine solution, and then 5 ml of 5·0M potassium hydroxide, and finally with 1 or 2 drops of the indicator solution. The solution was then titrated with 0·01250M EDTA prepared by weight from primary-standard grade disodium dihydrogen ethylenediaminetetra-acetate dihydrate. The titrations were carried out in the dark (in a box with an amber glass window[3]) under radiation from an ultraviolet source housed in a box with a slit; the assembly is shown in the recent text by Diehl.[4] Best results were obtained with the very minimum amount of indicator.

RESULTS AND DISCUSSION

It was surprising that the compound isolated was $K_2Ca_5Calcein_2$ rather than $K_2Ca_2Calcein$. The composition of the filtrate from the crop of solid was consonant with this, being deficient in calcium. Each molecule of Calcein binds two calcium ions, so the fifth calcium ion, like the two potassium ions, is ionic. That is, the character of the compound is probably expressed by $K_2Ca[Ca_2Calcein]_2$.

The periodic titration of calcium with EDTA, using the various indicator solutions, showed that Calcein prepared according to the original directions deteriorated within two days, producing sufficient background fluorescence to obscure the end-point; by holding the pH at 7, the deterioration could be reduced, such a solution being useful for seven or eight days. Calcein in 1:1 water–ethanol is much more stable but deterioration did occur with the development of background fluorescence and although the results of titrations even with indicator 60 days old were satisfactory the background fluorescence was gradually increasing. Solutions of Statocalcein showed no deterioration and no background fluorescence over a period of 210 days. The end-points were sharp, and in the darkened room, as distinctive as turning off a light bulb. The results of the analyses made on the stock solution of calcium chloride (using 60-day old indicators) were excellent, the precision being that expected in good volumetric work without precise temperature control, the average titre being 40·02 ml of 0·0125M EDTA for titrations with each of indicators (2), (3) and (4), the standard deviations being 0·06, 0·03 and 0·04 ml respectively for these indicators (11 determinations each).

Dept of Chemistry
Iowa State University
Ames, Iowa 50010, *U.S.A.*

William C. Hoyle
Harvey Diehl

Summary—A dipotassium pentacalcium dicalcein salt ("Statocalcein") is recommended for use in place of Calcein as an indicator for fluorimetric titration of calcium with EDTA. The new indicator remains stable in solution for long periods (at least 210 days).

Zusammenfassung—Ein Dikalium-pentacalcium-dicalceinsalz ("Statocalcein") wird anstelle von Calcein als Indikator zur fluorimetrischen Titration von Calcium mit EDTA empfohlen. Der neue Indikator ist in Lösung lange Zeit stabil (mindestens 210 Tage).

Résumé—On recommande un sel dipotassique pentacalcique de dicalcéine ("Statocalcéine") pour l'emploi à la place de la Calcéine en tant qu'indicateur pour le titrage fluorimétrique du calcium à l'EDTA. Le nouvel indicateur reste stable en solution pendant de longues périodes (au moins 210 jours).

REFERENCES

1. A. J. Hefley, *Ph.D. Thesis*, 1967. Iowa State University, Ames, Iowa, U.S.A. 50010.
2. H. Diehl and J. L. Ellingboe, *Anal. Chem.*, 1956, **28**, 882.
3. H. Diehl, *Calcein, Calmagite, and o,o'-Dihydroxyazobenzene. Titrimetric, Colorimetric and Fluorimetric Reagents for Calcium and Magnesium*, p. 25. G. Frederick Smith Chemical Company, Columbus, Ohio, 1963.
4. *Idem*, *Quantitative Analysis*, p. 286. Oakland Street Science Press, Ames, Iowa 1970.

Talanta, 1972, Vol. 19, pp. 208 to 209. Pergamon Press. Printed in Northern Ireland

Rapid determination of traces of silver in sulphide ores by atomic absorption

(*Received* 7 *June* 1971. *Accepted* 18 *July* 1971)

SPECTROPHOTOMETRIC methods using *p*-dimethylaminobenzylidenerhodanine[1,2] and dithizone[3] for the determination of small quantities of silver are not entirely satisfactory though widely used. However, atomic-absorption spectrophotometry offers rapidity and accuracy for determination trace quantities of silver. A method involving this technique developed by Rawling *et al.*[4] for determination of silver in lead concentrates recommends addition of ammonium acetate and potassium cyanide to sample solutions to keep both silver and lead in solution before aspiration into the flame. Rubeška *et al.*[5] adopted various methods of digestion for different sulphide minerals (galena, tetrahedrite, sphalerite and antimonites) and recommend the use of tartaric acid to prevent precipitation of antimony. In addition, mercury(II) nitrate was added to overcome the effect of chloride ions which tend to decrease the signal, owing to adsorption of silver chloride on the walls of the glass container. Greaves[6] made use of alkylpolyamines such as diethylenetriamine to keep both lead and silver dissolved as stable soluble chelates in 8*M* hydrochloric acid.

We have achieved excellent results by adding an excess of ammonia to the sample solution obtained by digestion with *aqua regia*, and aspirating this ammoniacal solution into the flame of an atomic absorption spectrophotometer. This method ensures retention of all the silver in a soluble state in the supernatant liquid while throwing down most of the metallic ions as hydroxides.

EXPERIMENTAL

Reagents

A 100-ppm standard silver solution was prepared by dissolving 0·1575 g of silver nitrate in 800 ml of demineralized water and adding 5% ammonia solution drop by drop till a clear solution was obtained, and finally diluting to 1000 ml; 10-ppm and 1-ppm standard solutions were prepared by diluting this solution with 1% ammonia solution. All other reagents were analytical-reagent grade.

Apparatus

A model AA 100 Tectron Atomic Absorption Spectrophotometer with ASL hollow-cathode lamp was used. The most sensitive silver absorption line at a wavelength of 328·1 nm was chosen to measure the absorbance values. The working conditions were:

Lamp current:	4 mA
Acetylene pressure:	10 psi, flow-meter reading 4·5
Air pressure	15 psi
Slit	0·10 mm

A standard 0·10-m stainless-steel AB 51 burner with a 0·5-mm wide slit was used.

Calibration

Portions (3 ml) of 10-ppm silver standard solution were diluted to 20 ml after addition of various amounts of ammonia solution (1 + 1), and the absorbances of the solutions were measured. From Table I, it can be seen that addition of at least 3 ml of the ammonia solution is required to produce maximum absorbance. The atomic absorbance values of 0, 0·5, 1·0, 1·5 and 2·0 ppm silver solutions containing 1 ml hydrochloric acid (1 + 1) and 5 ml of ammonia solution (1 + 1) in a total volume of 20 ml were measured and a calibration curve was drawn.

TABLE I.—EFFECT OF AMMONIA ON ATOMIC ABSORBANCE OF SILVER AT 328·1 nm

Ammonia solution, *ml*	Absorbance	Ammonia solution, *ml*	Absorbance
0·1	0·095	2·0	0·135
0·2	0·105	3·0	0·145
0·5	0·11	5·0	0·145
1·0	0·12	10·0	0·145

Procedure

A 0·1–0·2 g sample was weighed into a dry graduated cylinder (of a type which could be stoppered), 3ml of *aqua regia* were added and the mixture was digested on a hot-plate for about an hour. After cooling to room temperature the solution was neutralized by dropwise addition of ammonia solution (1 + 1) till a permanent precipitate of iron and other hydroxides formed. Then 5 ml of the ammonia solution were added and the mixture was made up to 20 ml. The cylinder was stoppered and after vigorous shaking the solution was allowed to settle for an hour. The supernatant liquid was aspirated into the flame and the absorbance recorded.

RESULTS

Fe(III), Al, Cr(III), Sb(III), Bi, As(III), Cu(II), Pb, Zn, Co(II), Ni, Hg(II), Sn(IV), V(V), Mo(VI), W(VI), Ca, Mg, Na, K, Cl^- and SO_4^{2-} in concentrations ranging between 0·5 and 2·5 mg/ml were found to cause no change in the absorbance of 1·5 ppm of silver. Addition of Sn(II) lowered the absorbance considerably because it separated silver from the ammoniacal silver nitrate solution. However if sufficient Fe^{3+} is present in solution (as is often the case) the Sn^{2+} is oxidized before the addition of ammonia, and does not interfere.

Apart from this interference from Sn^{2+}, the metal hydroxides precipitated by ammonia do not seem to retain any silver if a sufficient excess of ammonia is present. Copper, nickel, cobalt, cadmium and zinc remain in solution along with silver but do not cause any interference.

A large number of silver-bearing samples analysed by this method yielded values for silver in close agreement with those obtained by the potassium cyanide-ammonium acetate method.[4]

Central Laboratories
Airborne Mineral Surveys &
Exploration
Faridabad, Haryana, India

A. PURUSHOTTAM
S. S. LAL
P. P. NAIDU

Summary—The silver in sulphide ores is assayed by dissolution of the sample in *aqua regia*, addition of excess of ammonia solution and the measurement of the atomic absorbance of the supernatant solution at 328·1 nm.

Zusammenfassung—Das Silber in sulfidischen Erzen wird bestimmt durch Lösen der Probe in Königswasser, Zugabe von überschüssiger Ammoniaklösung und Messung der Atomabsorption der Lösung über dem Bodenkörper bei 328,1 nm.

Résumé—On dose l'argent dans les minerais sulfurés par dissolution de l'échantillon dans l'eau régale addition d'un excès de solution d'ammoniaque et mesure de l'absorption atomique de la solution surnageante à 328,1 nm.

REFERENCES

1. G. C. B. Cave and D. N. Hume, *Anal. Chem.*, 1952, **24**, 1503.
2. A. Ringbom and E. Linko, *Anal. Chim. Acta*, 1953 **9**, 80.
3. H. Freideberg, *Anal. Chem.*, 1955, **27**, 305.
4. B. S. Rawling, M. D. Amos and M. C. Greaves, *Proc. Australasian Inst. Mining Met.* 1961, **1**, 199.
5. I. Rubeška, Z. Šulcek and B. Moldan, *Anal. Chim. Acta*, 1967, **37**, 27.
6. M. C. Greaves, *Nature*, 1963, **199**, 552.

Talanta, 1972, Vol. 19, pp. 209 to 212. Pergamon Press. Printed in Northern Ireland

The absorption of carbon dioxide in solutions of monoethanolamine

(*Received* 30 *August* 1971. *Accepted* 15 *September* 1971)

ONE OF THE MORE POPULAR methods for the determination of carbon in steel and other materials involves combustion of the sample in a stream of oxygen and absorption and titration of the resulting carbon dioxide in non-aqueous media. A number of procedures have now been proposed which

Procedure

A 0·1–0·2 g sample was weighed into a dry graduated cylinder (of a type which could be stoppered), 3ml of *aqua regia* were added and the mixture was digested on a hot-plate for about an hour. After cooling to room temperature the solution was neutralized by dropwise addition of ammonia solution (1 + 1) till a permanent precipitate of iron and other hydroxides formed. Then 5 ml of the ammonia solution were added and the mixture was made up to 20 ml. The cylinder was stoppered and after vigorous shaking the solution was allowed to settle for an hour. The supernatant liquid was aspirated into the flame and the absorbance recorded.

RESULTS

Fe(III), Al, Cr(III), Sb(III), Bi, As(III), Cu(II), Pb, Zn, Co(II), Ni, Hg(II), Sn(IV), V(V), Mo(VI), W(VI), Ca, Mg, Na, K, Cl^- and SO_4^{2-} in concentrations ranging between 0·5 and 2·5 mg/ml were found to cause no change in the absorbance of 1·5 ppm of silver. Addition of Sn(II) lowered the absorbance considerably because it separated silver from the ammoniacal silver nitrate solution. However if sufficient Fe^{3+} is present in solution (as is often the case) the Sn^{2+} is oxidized before the addition of ammonia, and does not interfere.

Apart from this interference from Sn^{2+}, the metal hydroxides precipitated by ammonia do not seem to retain any silver if a sufficient excess of ammonia is present. Copper, nickel, cobalt, cadmium and zinc remain in solution along with silver but do not cause any interference.

A large number of silver-bearing samples analysed by this method yielded values for silver in close agreement with those obtained by the potassium cyanide-ammonium acetate method.[4]

Central Laboratories
Airborne Mineral Surveys &
Exploration
Faridabad, Haryana, India

A. Purushottam
S. S. Lal
P. P. Naidu

Summary—The silver in sulphide ores is assayed by dissolution of the sample in *aqua regia*, addition of excess of ammonia solution and the measurement of the atomic absorbance of the supernatant solution at 328·1 nm.

Zusammenfassung—Das Silber in sulfidischen Erzen wird bestimmt durch Lösen der Probe in Königswasser, Zugabe von überschüssiger Ammoniaklösung und Messung der Atomabsorption der Lösung über dem Bodenkörper bei 328,1 nm.

Résumé—On dose l'argent dans les minerais sulfurés par dissolution de l'échantillon dans l'eau régale addition d'un excès de solution d'ammoniaque et mesure de l'absorption atomique de la solution surnageante à 328,1 nm.

REFERENCES

1. G. C. B. Cave and D. N. Hume, *Anal. Chem.*, 1952, **24**, 1503.
2. A. Ringbom and E. Linko, *Anal. Chim. Acta*, 1953 **9**, 80.
3. H. Freideberg, *Anal. Chem.*, 1955, **27**, 305.
4. B. S. Rawling, M. D. Amos and M. C. Greaves, *Proc. Australasian Inst. Mining Met.* 1961, **1**, 199.
5. I. Rubeška, Z. Šulcek and B. Moldan, *Anal. Chim. Acta*, 1967, **37**, 27.
6. M. C. Greaves, *Nature*, 1963, **199**, 552.

Talanta, 1972, Vol. 19, pp. 209 to 212. Pergamon Press. Printed in Northern Ireland

The absorption of carbon dioxide in solutions of monoethanolamine

(*Received* 30 *August* 1971. *Accepted* 15 *September* 1971)

One of the more popular methods for the determination of carbon in steel and other materials involves combustion of the sample in a stream of oxygen and absorption and titration of the resulting carbon dioxide in non-aqueous media. A number of procedures have now been proposed which include both coulometric and volumetric addition of the titrant. An important condition of these methods is that the absorption of the carbon dioxide in the titration medium or titrand solution should be 100% efficient and the use of dilute solutions of monoethanolamine has been found satisfactory in many cases. One of the earlier groups of workers in this field, Blom *et al.*,[1] suggested that the efficiency of absorption of carbon dioxide by monoethanolamine solutions was due to the formation of 2-hydroxyethylcarbamic acid,

$$HO{\cdot}C_2H_4{\cdot}NH_2 + CO_2 \rightarrow HO{\cdot}C_2H_4{\cdot}NH{\cdot}COOH$$

but no evidence was put forward in support of this conclusion. A similar situation applies to the reactions of a number of other amines with carbon dioxide which have been explained on a similar basis.[2-5] Braid *et al.*[6] have reported some studies in which carbon dioxide was bubbled through pure amine solutions and the resulting syrupy liquids were examined by infrared spectroscopy. They concluded, 'It therefore seems likely that substituted ammonium carbamates are formed,' in agreement with an earlier suggestion by Smola.[2] Although the infrared evidence is useful, it is not conclusive and since it appears likely to be taken as establishing this reaction,[7] it seemed of some importance to attempt to obtain more precise information on the products of the reaction of carbon dioxide with, in particular, dilute solutions of monoethanolamine.

In the normal procedures for carbon analysis, monoethanolamine is used as a 0·5–5% v/v solution in pyridine[1,9] or dimethylformamide[6-8] and, under these conditions, no insoluble product separates out. To obtain the required information, two procedures were adopted. Slightly more concentrated solutions were taken (10%) and (*a*) strontium chloride was included to bring about precipitation of the strontium salt of the acid formed and (*b*) carbon dioxide was passed through a strontium-free solution for a long time, whereupon an oily phase separated out. The products from both (*a*) and (*b*) were analysed.

When carbon dioxide was bubbled into pyridine containing ethanolamine (10% v/v) and strontium chloride hexahydrate (5% w/v), a glutinous mass separated out which, after washing with pyridine and drying in a vacuum oven at 50°, gave a white solid which appeared to be strontium 2-hydroxyethylcarbamate contaminated with about 7% strontium carbonate and 6% strontium chloride. The use of the hydrate appeared to be the cause of the formation of strontium carbonate and, to avoid this contamination, the experiment was repeated with 3·5% w/v anhydrous strontium chloride solution. The material obtained (Compound A) was insoluble in water and readily decomposed by dilute mineral acids, evolving carbon dioxide, a characteristic property of carbamates. It was subjected to elemental microanalysis (Table I), thermogravimetric analysis (Fig. 1) and infrared analysis. The thermogravimetric curve shows three breaks. The weight loss up to 120° was due to loss of volatile material, presumably water absorbed by the sample after separation. The loss at 300° was 50% on a dry-weight basis and corresponds exactly to the loss expected from the reaction,

$$Sr(C_3H_6O_3N)_2 \xrightarrow{300^\circ} SrCO_3$$

The final weight loss, 29·5%, corresponds to the decomposition of the carbonate to the oxide,

$$SrCO_3 \xrightarrow{1000^\circ} SrO + CO_2$$

TABLE I.—COMPOSITION OF COMPOUNDS A AND B

(Theoretical figures are based on $Sr(C_3H_6O_3N)_2$ for A and $[HOC_2H_4NHCO_2]^-[H_3NC_2H_4OH]^+$ for B)

Compound		*Elemental analysis* Theory, %	Reported, %	Corrected, %	Atomic ratio
A	C	24·40	18·7	23·5	5·8
	H	4·06	4·5	4·3	12·5
	N	9·38	8·4	8·7	1·8
	Sr	29·70	28·6	29·7	1·0
	O	32·47	35·8*	33·8	6·2
B	C	36·16	36·8		5·2
	H	8·49	9·0		15·0
	N	16·88	16·7		2·0
	O	38·47	37·5*		3·9

* By difference.

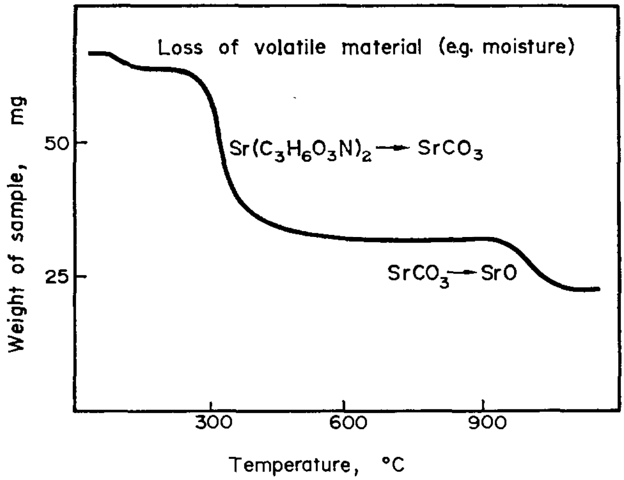


FIG. 1.—Thermolysis curve of compound A.

for which the theoretical weight loss is 29·8%. The thermogravimetric results show that strontium carbonate is formed at the temperature (800°) used for the ignition in the carbon determination and the carbon result will therefore be low. The thermogravimetric data also shows that 3·82% volatile material, presumed to be absorbed water, is present and difficult to exclude completely, owing to the hygroscopic nature of the material. Correction for both these errors is a simple matter and the corrected figures given in Table I are in reasonable agreement with the theoretical composition for $Sr(C_3H_6O_3N)_2$. Slight discrepancies are almost certainly due to small variations in the water content between different analyses.

Passing carbon dioxide through a 90:10 mixture of pyridine and ethanolamine in the *absence of strontium chloride* yielded a viscous oily phase (Compound B) which separated out at the bottom of the reaction vessel. This was also hygroscopic, was readily soluble in water and was also decomposed by dilute mineral acids with evolution of carbon dioxide. The material also appeared to give a pale violet fluorescence. The elemental analysis of Compound B is also given in Table I and suggests that it is in fact the monoethanolamine salt of 2-hydroxyethylcarbamic acid.

Infrared spectra of both Compound B and monoethanolamine itself were obtained from thin liquid films between KBr discs and that of Compound A from a pressed KBr pellet. All three spectra were generally similar but new bands were observed for both A and B in the region 1600–1300 cm^{-1} and at 800–850 cm^{-1}. These were in general agreement with the reported results of Braid *et al.*,[6] although less detail was observable in our case, possibly due to contamination by pyridine. Thus, the band at 1600 cm^{-1} in ethanolamine disappears and new bands appear at 1580 and 1390 cm^{-1}, as be expected for an ionized carboxyl group. The infrared evidence is not, however, particularly conclusive on its own.

CONCLUSION

It is established that the acidic species present in solutions of ethanolamine in pyridine after the absorption of carbon dioxide is the ethanolamine salt of 2-hydroxyethylcarbamic acid. This compound and the strontium salt of 2-hydroxyethylcarbamic acid have both been isolated from this medium and identified. As has been assumed previously, it is this acid which is titrated on addition of a strong base to the solution. Amines such as monoethanolamine therefore provide excellent absorption properties for carbon dixoide. The existence of the chemical reaction instead of simple dissolution means that the carbon dioxide is not easily removed, *e.g.*, by continued flushing of oxygen through the solution, and is available in acidic form for titration with bases.

Acknowledgement—The authors are indebted to Mr. F. Daubney for the microanalytical results for C, H and N given in Table I.

Department of Pure and Applied Chemistry
University of Strathclyde
Cathedral Street
Glasgow, C.1

D. W. WHYMARK*
J. M. OTTAWAY

---

* Present address: Fisons Ltd., Pharmaceuticals Division, Bakewell Road, Loughborough, Leicestershire.

Summary—Infrared, thermogravimetric and analytical results are presented that establish that the ethanolamine salt of 2-hydroxyethylcarbamic acid is formed when carbon dioxide is absorbed in solutions of ethanolamine.

Zusammenfassung—Es werden Ergebnisse von Infrarotmessungen, Thermogravimetrie und Analysen vorgelegt, die zeigen, daß bei der Absorption von Kohlendioxid in Äthanolaminlösungen das Äthanolaminsalz der 2-Hydroxycarbaminsäure gebildet wird.

Résumé—On présente des résultats d'infra-rouge, thermogravimétriques et analytiques qui établissent qu'il se forme le sel d'éthanolamine de l'acide 2-hydroxycarbamique lorsque le gaz carbonique est absorbé dans des solutions d'éthanolamine.

REFERENCES

1. L. Blom, L. Edelhausen and T. Smeets, *Z. Anal. Chem.*, 1962, **189**, 91.
2. A. Smola, *Mitt. Chem. Forsch.—Inst. Ind. Oestr.*, 1948, **2**, 38.
3. F. Fichter and B. Becker, *Ber.*, 1911, **44**, 3481.
4. M. Frankel and E. Katchalski, *J. Am. Chem. Soc.*, 1943, **65**, 1670.
5. H. B. Wright and M. B. Moore, *ibid.*, 1948, **70**, 3865.
6. P. Braid, J. A. Hunter, W. H. S. Massie, J. D. Nicholson and B. E. Pearce, *Analyst*, 1966, **91**, 439.
7. H. J. Boniface and R. H. Jenkins, *ibid.*, 1971, **96**, 37.
8. R. F. Jones, P. Gale, H. Hopkins and L. N. Powell, *ibid.*, 1965, **90**, 623.
9. J. M. Ottaway, D. W. Whymark, B. Metters, and B. G. Cooksey, *Talanta*, 1971, **18**, 773.

Talanta, 1972, Vol. 19, pp. 212 to 214. Pergamon Press. Printed in Northern Ireland

Oxidimetric determination of ascorbic acid with potassium hexacyanoferrate(III) in acid medium

(*Received* 21 *April* 1971, *Revised* 20 *August* 1971. *Accepted* 4 *October* 1971)

According to Kolthoff and Belcher[1] hexacyanoferrate(III) is obtainable in a high state of purity and serves as its own primary standard. It is a convenient oxidimetric reagent because of its stability in aqueous solution and its large equivalent weight. It is mostly employed for the determination of organic substances in neutral or alkaline media. It has been used for the determination of ascorbic acid by Hubicka[2] at pH 7, employing an amperometric technique and by van Pinxteren and Verloop[3] with a dead-stop end-point procedure in bicarbonate medium. Erdey and Svehla[4] proposed the visual titration of ascorbic acid with this reagent in a slightly alkaline medium buffered with sodium acetate, using 2,6-dichlorophenolindophenol as redox indicator. In an attempt to determine the redox potentials of the ascorbic acid $\rightleftharpoons$ dehydroascorbic acid system from potentiometric titration curves, Ball[5] reported that at pH 5 not only ascorbic acid but also dehydroascorbic acid reduces hexacyanoferrate(III). Abramov and Kadyrov[6] proposed the indirect determination in a slightly acid medium. After an aliquot of the ascorbic acid solution was reacted with a known and excessive amount of hexacyanoferrate(III) in the presence of zinc sulphate, the unreacted oxidant was treated with an excess of potassium iodide and the iodine liberated titrated with sodium thiosulphate, with starch as indicator. Sant[7] improved the method by direct titration in a medium buffered with zinc acetate to pH 6, with a starch-iodide end-point. In both cases, the zinc salt raises the redox potential of the hexacyanoferrate system towards the end-point by precipitating the hexacyanoferrate(II). At the higher pH the titration is likely to be vitiated by the reaction of dehydroascorbic acid with the oxidizing titrant, as stated by Ball. We have, therefore, undertaken this investigation to ascertain the conditions under which potassium hexacyanoferrate(III) can be used for the direct titration of ascorbic acid in acid medium with visual and potentiometric end-points.

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III) solution, 0·1*N*. Stored in an amber bottle, and diluted as required.

Summary—Infrared, thermogravimetric and analytical results are presented that establish that the ethanolamine salt of 2-hydroxyethylcarbamic acid is formed when carbon dioxide is absorbed in solutions of ethanolamine.

Zusammenfassung—Es werden Ergebnisse von Infrarotmessungen, Thermogravimetrie und Analysen vorgelegt, die zeigen, daß bei der Absorption von Kohlendioxid in Äthanolaminlösungen das Äthanolaminsalz der 2-Hydroxycarbaminsäure gebildet wird.

Résumé—On présente des résultats d'infra-rouge, thermogravimétriques et analytiques qui établissent qu'il se forme le sel d'éthanolamine de l'acide 2-hydroxycarbamique lorsque le gaz carbonique est absorbé dans des solutions d'éthanolamine.

REFERENCES

1. L. Blom, L. Edelhausen and T. Smeets, *Z. Anal. Chem.*, 1962, **189**, 91.
2. A. Smola, *Mitt. Chem. Forsch.—Inst. Ind. Oestr.*, 1948, **2**, 38.
3. F. Fichter and B. Becker, *Ber.*, 1911, **44**, 3481.
4. M. Frankel and E. Katchalski, *J. Am. Chem. Soc.*, 1943, **65**, 1670.
5. H. B. Wright and M. B. Moore, *ibid.*, 1948, **70**, 3865.
6. P. Braid, J. A. Hunter, W. H. S. Massie, J. D. Nicholson and B. E. Pearce, *Analyst*, 1966, **91**, 439.
7. H. J. Boniface and R. H. Jenkins, *ibid.*, 1971, **96**, 37.
8. R. F. Jones, P. Gale, H. Hopkins and L. N. Powell, *ibid.*, 1965, **90**, 623.
9. J. M. Ottaway, D. W. Whymark, B. Metters, and B. G. Cooksey, *Talanta*, 1971, **18**, 773.

Talanta, 1972, Vol. 19, pp. 212 to 214. Pergamon Press. Printed in Northern Ireland

Oxidimetric determination of ascorbic acid with potassium hexacyanoferrate(III) in acid medium

(*Received* 21 *April* 1971, *Revised* 20 *August* 1971. *Accepted* 4 *October* 1971)

ACCORDING to Kolthoff and Belcher[1] hexacyanoferrate(III) is obtainable in a high state of purity and serves as its own primary standard. It is a convenient oxidimetric reagent because of its stability in aqueous solution and its large equivalent weight. It is mostly employed for the determination of organic substances in neutral or alkaline media. It has been used for the determination of ascorbic acid by Hubicka[2] at pH 7, employing an amperometric technique and by van Pinxteren and Verloop[3] with a dead-stop end-point procedure in bicarbonate medium. Erdey and Svehla[4] proposed the visual titration of ascorbic acid with this reagent in a slightly alkaline medium buffered with sodium acetate, using 2,6-dichlorophenolindophenol as redox indicator. In an attempt to determine the redox potentials of the ascorbic acid ⇌ dehydroascorbic acid system from potentiometric titration curves, Ball[5] reported that at pH 5 not only ascorbic acid but also dehydroascorbic acid reduces hexacyanoferrate(III). Abramov and Kadyrov[6] proposed the indirect determination in a slightly acid medium. After an aliquot of the ascorbic acid solution was reacted with a known and excessive amount of hexacyanoferrate(III) in the presence of zinc sulphate, the unreacted oxidant was treated with an excess of potassium iodide and the iodine liberated titrated with sodium thiosulphate, with starch as indicator. Sant[7] improved the method by direct titration in a medium buffered with zinc acetate to pH 6, with a starch-iodide end-point. In both cases, the zinc salt raises the redox potential of the hexacyanoferrate system towards the end-point by precipitating the hexacyanoferrate(II). At the higher pH the titration is likely to be vitiated by the reaction of dehydroascorbic acid with the oxidizing titrant, as stated by Ball. We have, therefore, undertaken this investigation to ascertain the conditions under which potassium hexacyanoferrate(III) can be used for the direct titration of ascorbic acid in acid medium with visual and potentiometric end-points.

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(III) solution, 0·1*N*. Stored in an amber bottle, and diluted as required.

Ascorbic acid solution, 0·1*N*. Stabilized with a small amount of sulphuric acid, and standardized against potassium iodate. Diluted as required and standardized with iodate.

Demineralized water was used throughout because of the decomposition of ascorbic acid by traces of metallic impurities.

Visual titration in sulphuric acid medium

Oxidation of barium diphenylaminesulphonate by hexacyanoferrate(III) is rapid only when the sulphuric acid concentration is greater than 4*M* and reduction of oxidized indicator by ascorbic acid is rapid at all sulphuric acid concentrations $<5M$ but retarded at concentrations $>5M$. For this reason the range of acidity for titration should be 4–5*M* at the equivalence point. To 40 ml of 8*M* sulphuric acid in a 250-ml conical flask add 3–8 ml ascorbic acid solution and 1 drop of 0·2% solution barium diphenylaminesulphonate and titrate with hexacyanoferrate(III). The equivalence point is heralded by transient appearance of a violet colour. Towards the equivalence point, the titrant is added dropwise at 3–4 sec. intervals. The end-point is indicated by a violet colour stable for 2–3 min. At low ascorbic acid concentration (20–200 μg/ml) the consumption of hexacyanoferrate(III) is low by 1–2% because of aerial oxidation of the ascorbic acid, but the results are accurate if a carbon dioxide atmosphere is used and an indicator correction of 0·02 ml of 0·01*M* titrant is deducted. No inert atmosphere is necessary for more concentrated solutions. Typical results are given in Table I.

TABLE I.—TITRIMETRIC DETERMINATION OF ASCORBIC ACID WITH HEXACYANOFERRATE(III)

Amount of ascorbic acid, *mg*			
Taken	Found	Taken	Found
72·74	72·70	8·166	8·167
57·73	57·61	7·705	7·691
48·21	48·39	6·742	6·751
43·42	43·25	5·780	5·792
36·38	36·47	5·154	5·140
25·14	25·18	3·992	3·987
		3·280	3·284
		1·919	1·920

Interferences

A tenfold excess of oxalic, citric, tartaric, succinic, malic and acetic acids, and glucose, fructose and sucrose does not interfere.

Visual titrations in other acidic media

Similar results are obtained in 7–10*M* hydrochloric acid or 9·0–11·0*M* phosphoric acid. The end point is sluggish (10–30 sec between additions) in phosphoric acid medium, but an advantage is that even dilute solutions of ascorbic acid (0·005*M*) can be titrated in air.

TABLE II.—POTENTIOMETRIC TITRATION OF ASCORBIC ACID WITH HEXACYANOFERRATE(III) IN 10*M* PHOSPHORIC ACID

Amount of ascorbic acid, *mg*	
Taken	Found
24·13	24·22
29·44	29·44
38·71	38·55
48·78	48·78
58·02	57·76
66·95	66·95
73·55	73·47

Potentiometric titrations

For potentiometric titration a bright platinum rod is used as indicator electrode and a saturated calomel cell as reference electrode. In 4·5–5·5M sulphuric acid medium the potential stabilizes within 1 min in the early stages and 5 min at the end-point. The potential break is 100–120 mV per drop (0·04 ml) of 0·1N hexacyanoferrate(III), but the end-point is 1–2% lower than the true equivalence point. However, with rapid titration in an inert atmosphere and immediate reading of potential in the early stages and a wait of 1 min before readings near the end-point, an inflexion occurs at the true equivalence point. This implies that in a slow titration some aerial oxidation occurs.

Potentiometric titration in 10–12M phosphoric acid gives an end-point that corresponds to the true equivalence point and there is no need to maintain an inert atmosphere. Table II shows the relative error is 0·4%. The results are not affected by the presence of a 10–20 fold excess of sucrose, dextrose, citric acid, tartaric acid, malic acid and oxalic acid.

Department of Chemistry
Andhra University
Waltair, S. India

G. SITARAMA SASTRY
G. GOPALA RAO

Summary—Conditions have been developed for the titrimetric determination of ascorbic acid with hexacyanoferrate(III), with potentiometric and visual end-points, in sulphuric, hydrochloric or phosphoric acid media. Several organic substances likely to be present in plant tissues do not interfere.

Zusammenfassung—Die Bedingungen zur titrimetrischen Bestimmung von Ascorbinsäure mit Hexacyanoferrat(III) mit potentiometrischer oder visueller Endpunktsbestimmung in schwefelsaurem, salzsaurem oder phosphorsaurem Medium wurden ermittelt. Mehrere organische Substanzen, die in Pflanzengeweben wahrscheinlich vorkommen, stören bei der Bestimmung nicht.

Résumé—On a mis au point les conditions du dosage titrimétrique de l'acide ascorbique au moyen d'hexacyanoferrate(III), avec points de fin de dosage potentiométrique et visuel, en milieux acide sulfurique, chlorhydrique ou phosphorique. Plusieurs substances organiques susceptibles d'être présentes dans les tissus végétaux n'interfèrent pas.

REFERENCES

1. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III p. 645. Interscience, New York, 1957.
2. K. Hubicka, *Ann. Univ. Mariae Curie-Sklodowska, Lublin-Polonia, Sect. AA*, 1957, **10**, 35.
3. J. A. C. van Pinxteren and E. Verloop, *Pharm. Weekblad*, 1958, **23**, 203, 982, *Anal. Abstr.*, 1959, **6**, 3230.
4. L. Erdey and G. Svehla, *Z. Anal. Chem.*, 1956, **150**, 407.
5. E. G. Ball, *J. Biol. Chem.*, 1937, **118**, 219.
6. M. K. Abramov and Ya. K. Kadyrov, *Aptechnoe Delo*, 1956, **5**(2), 28; *Anal., Abstr.*, 1957, **4**, 283.
7. B. R. Sant, *Chemist-Analyst*, 1958, **47**, 65.

Talanta, 1972, Vol. 19, pp. 214 to 217. Pergamon Press. Printed in Northern Ireland

Microtitrimetric determination of uranium in nitric acid medium in the presence of excess of iron, magnesium and aluminium

(*Received* 15 *March* 1971. *Revised* 5 *July* 1971. *Accepted* 30 *August* 1971)

DAVIES AND GRAY[1] developed a method for titration of uranium(VI) with iron(II) in phosphoric acid medium after reduction to U(IV) and eliminated the interference of nitrate. Their method also avoids the sluggishness of reaction near the end-point that is experienced with the Rao and Sagi method.[2] The Davies and Gray procedure was developed for 200–300 mg amounts of uranium, and has since been

Potentiometric titrations

For potentiometric titration a bright platinum rod is used as indicator electrode and a saturated calomel cell as reference electrode. In 4·5–5·5*M* sulphuric acid medium the potential stabilizes within 1 min in the early stages and 5 min at the end-point. The potential break is 100–120 mV per drop (0·04 ml) of 0·1*N* hexacyanoferrate(III), but the end-point is 1–2% lower than the true equivalence point. However, with rapid titration in an inert atmosphere and immediate reading of potential in the early stages and a wait of 1 min before readings near the end-point, an inflexion occurs at the true equivalence point. This implies that in a slow titration some aerial oxidation occurs.

Potentiometric titration in 10–12*M* phosphoric acid gives an end-point that corresponds to the true equivalence point and there is no need to maintain an inert atmosphere. Table II shows the relative error is 0·4%. The results are not affected by the presence of a 10–20 fold excess of sucrose, dextrose, citric acid, tartaric acid, malic acid and oxalic acid.

Department of Chemistry
Andhra University
Waltair, S. India

G. Sitarama Sastry
G. Gopala Rao

Summary—Conditions have been developed for the titrimetric determination of ascorbic acid with hexacyanoferrate(III), with potentiometric and visual end-points, in sulphuric, hydrochloric or phosphoric acid media. Several organic substances likely to be present in plant tissues do not interfere.

Zusammenfassung—Die Bedingungen zur titrimetrischen Bestimmung von Ascorbinsäure mit Hexacyanoferrat(III) mit potentiometrischer oder visueller Endpunktsbestimmung in schwefelsaurem, salzsaurem oder phosphorsaurem Medium wurden ermittelt. Mehrere organische Substanzen, die in Pflanzengeweben wahrscheinlich vorkommen, stören bei der Bestimmung nicht.

Résumé—On a mis au point les conditions du dosage titrimétrique de l'acide ascorbique au moyen d'hexacyanoferrate(III), avec points de fin de dosage potentiométrique et visuel, en milieux acide sulfurique, chlorhydrique ou phosphorique. Plusieurs substances organiques susceptibles d'être présentes dans les tissus végétaux n'interfèrent pas.

REFERENCES

1. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III p. 645. Interscience, New York, 1957.
2. K. Hubicka, *Ann. Univ. Mariae Curie-Sklodowska, Lublin-Polonia, Sect. AA*, 1957, **10**, 35.
3. J. A. C. van Pinxteren and E. Verloop, *Pharm. Weekblad*, 1958, **23**, 203, 982, *Anal. Abstr.*, 1959, **6**, 3230.
4. L. Erdey and G. Svehla, *Z. Anal. Chem.*, 1956, **150**, 407.
5. E. G. Ball, *J. Biol. Chem.*, 1937, **118**, 219.
6. M. K. Abramov and Ya. K. Kadyrov, *Aptechnoe Delo*, 1956, **5**(2), 28; *Anal., Abstr.*, 1957, **4**, 283.
7. B. R. Sant, *Chemist-Analyst*, 1958, **47**, 65.

Talanta, 1972, Vol. 19, pp. 214 to 217. Pergamon Press. Printed in Northern Ireland

Microtitrimetric determination of uranium in nitric acid medium in the presence of excess of iron, magnesium and aluminium

(*Received* 15 *March* 1971. *Revised* 5 *July* 1971. *Accepted* 30 *August* 1971)

Davies and Gray[1] developed a method for titration of uranium(VI) with iron(II) in phosphoric acid medium after reduction to U(IV) and eliminated the interference of nitrate. Their method also avoids the sluggishness of reaction near the end-point that is experienced with the Rao and Sagi method.[2] The Davies and Gray procedure was developed for 200–300 mg amounts of uranium, and has since been applied to smaller amounts.[3-6] However, our attempts to scale it down (by a factor of 20) to cover submilligram levels were not immediately successful, and this paper describes the modifications found necessary.

EXPERIMENTAL

Reagents

These were the same as for the Davies and Gray method[1] except that 0·005*N* potassium dichromate was also used, and was prepared by dilution of the 0·05*N* reagent and standardized by titration of uranium.

Orthophosphoric acid, analytical-reagent grade

Procedures

A—for 0·1–3·0 mg of U
B—for 0·02–0·3 mg of U

Transfer 100 μl of sample (in 0–9*M* nitric acid) to a tall 50-ml beaker and dilute to 500 μl with water. Add 0·25 ml of 1·5*M* sulphamic acid, 2 ml of 85% orthophosphoric acid and 0·25 ml of 1*M* ferrous sulphate, mixing thoroughly after each addition (magnetic stirrer). Some sulphamic acid settles out after addition of the phosphoric acid, and after a while a fine, green, layer of U(IV) appears at the surface if there is more than 300 μg of U present. Add 0·5 ml of 4·0*M* nitric acid–0·1*M* sulphamic acid mixture and stir; the sulphamic acid precipitate then redissolves. Add 0·15 ml of 1% ammonium molybdate reagent and stir till the reaction mixture becomes grey, then stop the stirring and let the reaction take place. Bubbles evolve from the dark brown solution, and nitrous gases can be smelt. When the reaction is over (2–5 min) no bubbles are evolved and the solution is green or colourless. Immediately stir twice for 30-sec periods with a short (~1 min) break in between. After the first stirring, intensive evolution of N_2 and/or NO bubbles from the solution takes place; after the second, the evolution of bubbles is less intensive or only sporadic. Then add 1·25 ml of 9*M* sulphuric acid and stir similarly for two 30-sec periods. Immediately before the titration dilute the reaction mixture with 10·0 ml of distilled water and add 0·10 ml of 0·04% barium diphenylamine-sulphonate indicator solution. No nitrogen bubbles should evolve from the solution at this stage and any remaining crystals at the bottom are dissolved. Stirring continuously, titrate the solution with 0·05*N* dichromate (*A*) or 0·005*N* dichromate (*B*) from a 0·5-ml microburette till an intense red-purple colour persists for 1 min without fading.

In the proximity of the end-point it is necessary to wait after each addition of titrant, to see whether the solution is decolorized.

DISCUSSION AND RESULTS

Effect of orthophosphoric acid

The reduction of U(VI) to U(IV) by ferrous sulphate is quantitative in phosphoric acid medium if the phosphoric acid concentration exceeds 9·8*M*.[2] Scaling down of the Davies and Gray method should permit use of up to 0·75 ml of sample but it was found that high results were obtained. The safe limit is 0·5 ml of sample, if 85% orthophosphoric acid is used.

Effect of nitric acid

In the sample aliquot. According to Davies and Gray the permissible amount of nitrate in the sample aliquot is 50 mmole. According to Lindner *et al.*[3] the concentration of nitric acid in the sample should be 2–3*M*. Eberle *et al.*[6] consider that 3 g of nitrate can be tolerated in 15 ml of sample provided <1 mg of molybdenum is present. Under our experimental conditions, satisfactory results were obtained for 0·5-ml samples in which the concentration of nitric acid was 0·5–1·8*M*; low results were obtained for nitric acid concentrations between 1·8 and 6*M*.

In oxidation of excess of Fe(II). The most suitable means[1] of destroying the excess of Fe(II) is oxidation with nitric acid in the presence of molybdenum.[7] The optimum conditions require a certain range of nitric acid concentration in the reaction mixture, achieved by adding a constant volume of nitric acid–sulphamic acid mixture.

The limitation imposed by the need to have less than 0·9 mmole of nitrate present from the initial sample was dealt with by taking 100 μl of sample and diluting it to 500 μl before addition of the reagents. In this way the initial sample could be up to 9*M* in nitric acid, and the procedure was satisfactory for 0·5–9*M* nitric acid. If the nitric acid concentration was below 0·5*M*, however, the oxidation of excess of iron(II) became very slow (20–30 min), and it was found necessary to increase the amount of nitric acid–sulphamic acid reagent by 100% and of molybdate by 50% to make the oxidation sufficiently rapid. The method was then applicable even in the absence of nitric acid in the sample.

The disappearance of the dark brown colour of the nitrosyl iron(II) complex, and the removal of nitric oxide from the solution (which we think is very important) can be accelerated by efficient stirring. Short sharp bursts of stirring were found most effective, and necessary to prevent unwanted oxidation of uranium(IV). We had found that in the Davies and Gray procedure nitrogen bubbles were evolved during the beginning of the titration, and that although evolution of nitrogen had apparently ceased after the recommended standing time, stirring caused an intense release of gas bubbles. To us, this indicated the presence of unreacted nitrous acid or nitrite at the beginning of the titration, or the presence of at least traces of nitric oxide. Such a possibility does not seem to have considered earlier,[1,3] but the presence of nitric oxide or nitrous acid could cause oxidation of uranium-(IV) according to Slade's mechanism:[8]

$$U^{4+} + NO_3^- + H_2O \rightarrow UO_2^{2+} + HNO_2 + H^+ \qquad (1)$$

$$U^{4+} + 2\,HNO_2 \rightarrow UO_2^{2+} + 2\,NO + 2\,H^+ \qquad (2)$$

$$2\,NO + HNO_3 + H_2O \rightarrow 3\,HNO_2 \qquad (3)$$

In nitric acid medium uranium(IV) is oxidized slowly at first because (1) is very slow, but the rates of the autocatalytic reactions (2) and (3) are high, and some uranium(IV) will be oxidized if the NO or HNO_2 is not removed or destroyed. The reaction of nitrous acid with sulphamic acid is likely to be slower at low concentrations, so we considered it best to try to remove NO by vigorous stirring, to prevent reaction (3) from occurring, and the method proved successful.

Titration conditions

Scaling down of the Davies and Gray procedure by a factor of 20 gave satisfactory results. Dilution with more water, or use of more indicator, gave positive errors of up to 5%.

Cherry[9] has described an amperometric end-point method that was reported to give better precision and accuracy. Eberle *et al.*[6] found that addition of a vanadyl salt sharpened the end-point and improved the precision and accuracy.

Time factors

To avoid aerial or other oxidation of uranium(IV) the earlier methods[1,3,6] specify time schedules, especially for the period between destruction of excess of iron(II) and completion of the titration. This can constitute a problem if several analyses are to be done together. However, we have found the presence of excess of iron(II) prevents the oxidation of uranium(IV) for at least 2 hr; contrary to Lindner's statement,[3] individual treatment of each sample after this stage is not necessary at all, if the procedure proposed above is followed.

Effect of other ions

In the determination of 2·4 mg of uranium, the presence of 2·7 mg of aluminium, 2·4 mg of magnesium, and 11 mg of iron(II) and 0·5 mg of molybdenum(VI) in addition to the amounts added as reagents, caused errors of less then ±1·5%. The effect of other ions was described earlier.[1]

Accuracy and precision

By procedure *A*, 8 replicate samples containing 2440 μg uranium gave a mean of 2442 μg (range 2404–2478 μg). By procedure *B*, the error was less than 2 μg for 120–240 μg of uranium, but increased to 4 μg for 24–48 μg in the sample. The end-point was more difficult to detect when these low concentrations were used. No blank correction was found necessary; when blanks were determined they were found to be less than the average error.

Nuclear Research Institute, ČSAV
Řež near Prague, Czechoslovakia

V. MAREŠKA

Summary—The Davies and Gray procedure for determination of uranium in presence of nitric acid has been scaled down to permit the analysis of solutions 0–9*M* in nitric acid and containing 20–3000 μg of uranium. The original method required modification in the scaled-down version, the main alterations being removal of NO by rapid stirring during the oxidation of excess of iron(II), and an increase in the amount of two of the reagents. Several analyses can be done together.

Zusammenfassung—Die Methode von Davies und Gray zur Bestimmung von Uran in Gegenwart von Salpetersäure kann auf kleinere Mengen angewandt werden. Man kann dann 0–9*M* salpetersaure Lösungen mit 20–3000 μg Uran analysieren. Die Anwendung auf kleinere Mengen bedingt Änderungen der Originalmethode: die wichtigsten sind Entfernen von NO durch rasches Rühren während der Oxidation von überschüssigem Eisen(II) sowie größere Mengen von zwei Reagentien. Man kann mehrere Analysen zugleich ausführen.

Résumé—La technique de Davies et Gray pour le dosage de l'uranium en présence d'acide nitrique a été réduite à plus petite échelle pour permettre l'analyse de solutions 0–9 *M* en acide nitrique et contenant 20–3000 μg d'uranium. La mé'hode originale a nécessité des modifications dans la version à échelle réduite, les principaux remaniements étant l'élimination deNO par agitation rapide pendant l'oxydation de l'excès de fer (II), et un accroissement de la quantité de deux des réactifs. Plusieurs analyses peuvent être menées en même temps.

REFERENCES

1. W. Davies and W. Gray, *Talanta*, 1964, **11**, 1203.
2. G. G. Rao and S. R. Sagi, *ibid.*, 1962, **9**, 715.
3. L. Lindner and A. von Baeckmann, *Kernforschungszentrum Rept.*, KFK 701-EUR 3714d, Karlsruhe, Nov. 1967, AK-92-1-1.
4. M. J. Maurice, L. M. Angeletti and K. Buijs, *ibid.*, EUR 4133e, Karlsruhe, 1969.
5. G. R. Quidotti, in V. Pompei, V. Altamura, A. Canonico, *Com. Naz. Energ. Nucl.*, 1969, RT-CHI, 12.
6. A. R. Eberle, M. W. Lerner, C. G. Goldbeck and C. J. Rodden, IAEA Symposium, Karlsruhe, July 1970, Report SM-133/43.
7. I. M. Kolthoff, E. B. Sandell and B. Moskowitz, *J. Am. Chem. Soc.*, 1933, **55**, 1954.
8. A. L. Slade, *U.S. At. Energy Comm. Rept.* DP-554 (1961), from E. R. Schmid, *Mikrochim. Acta*, 1970, 301.
9. J. Cherry, *U.K. At. Energy Authority Prod. Group PG Rept.* 827(W), 1968.

Talanta, 1972, Vol. 19, pp. 219 to 262. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

SYNTHETIC INORGANIC ION-EXCHANGERS—I

HYDROUS OXIDES AND ACIDIC SALTS OF MULTIVALENT METALS

V. VESELÝ and V. PEKÁREK†
Nuclear Research Institute of the Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia

(*Received* 22 *March* 1971. *Accepted* 12 *September* 1971)

Summary—An exhaustive literature survey is given of the hydrous oxides and acidic salts of multivalent metals that are used as ion-exchange materials, the survey covering the preparation, properties, uses and theory of these materials.

DURING the last 10–15 years the inorganic ion-exchangers have firmly occupied their own position among the ion-exchange materials. A rapid development in nuclear energy, hydrometallurgy of rare elements, preparation of high-purity materials, water purification, *etc.*, has enforced attempts to find and synthesize new, highly selective ion-exchanging materials resistant to chemicals, temperature changes and radiation, and of more convenient properties than commercial organic or natural inorganic (soils, clay minerals, *etc.*) ion-exchangers.

A large number of synthetic inorganic substances has been described which exhibit ion-exchanging properties. These materials may be divided into the following main groups:

1. Hydrous oxides
2. Acidic salts of multivalent metals
3. Salts of heteropolyacids
4. Insoluble ferrocyanides
5. Synthetic aluminosilicates
6. Certain other substances, *e.g.*, synthetic apatites, sulphides, alkaline earth sulphates

A large number of papers dealing with the ion-exchange properties of these substances has been published. The excellent book by Amphlett[1] and the reviews by Churms[2] and Materova *et al.*[3] have covered this field up to 1964–5. However, during the last five years great progress has been made in development and study of the basic properties of these materials. We found it reasonable to review the papers appearing within the period 1965–70, with an attempt to cover the data published by the end of 1970. The present review is divided into two parts, the first covering hydrous oxides and acidic salts of multivalent metals, which have been the most intensively studied groups of synthetic inorganic ion-exchangers. The ion-exchange properties of the other substances will be reviewed in the second part.

---

* For copies of this Review see Publisher's announcement near the end of the issue.

† Present address: Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia.

HYDROUS OXIDES

The adsorptive properties of hydrous oxides, such as alumina, silica and ferric oxide have been known for many years and it has been established that the adsorption of ions by them is presumably by ion-exchange. In that sense the hydrous oxides are of particular interest because most of them can function both as cation and anion-exchangers, and under certain conditions both cation and anion-exchange can occur simultaneously. These substances are mostly amphoteric and their dissociation may be schematically represented as follows:

$$\text{M—OH} \rightleftharpoons \text{M}^+ + \text{OH}^- \qquad \text{(I)}$$

$$\text{M—OH} \rightleftharpoons \text{M—O}^- + \text{H}^+ \qquad \text{(II)}$$

(M represents the central atom)

Scheme **I** is favoured by acid conditions, when the substance can function as an anion-exchanger, and scheme **II** by alkaline conditions, when the substance can function as a cation-exchanger. Near the isoelectric point of the oxide,[2] dissociation according to both schemes can take place and both types of exchange may occur simultaneously.

A large number of compounds of this type has been studied in recent years,[1,2,4] some more extensively than others, with particular attention to deeper knowledge of the adsorption mechanism as well as to their application in chemical processing of radioactive materials and in water desalination processes. The progress during the last five years in studying the exchange properties of hydrous oxides will be reviewed in this section.

Hydrous oxides of bi- and tervalent metals

Hydrous oxides of bivalent metals

This group of exchangers includes hydroxides of Be^{2+}, Mg^{2+}, Zn^{2+} and their mixtures with ferric hydroxide and hydrous alumina.

Hydrous BeO of composition $BeO.1{\cdot}7H_2O$ acts both as cation and anion-exchanger[5,6] with the selectivity for alkali metal cations following the order of decreasing ionic radii of the unhydrated ions.[6] Magnesium hydroxide exhibits anion-exchange properties.[5] However, there has also been found an adsorption of Zn^{2+}, which is more co-precipitation within the $Mg(OH)_2$ than ion-exchange. The adsorption process obeys the Langmuir equation and in the case of large amounts of the adsorbate, a sigmoid isotherm was verified.[7] Very interesting phenomena were observed for mixed hydrous oxides. The adsorption isotherm of a mechanical mixture of $Mg(OH)_2$–2 $Fe(OH)_3$ was a superposition of the isotherms of both pure oxides and its hysteresis loop consisted of two parts, the first corresponding to coarse pores of $Mg(OH)_2$, and the second to fine pores of $Fe(OH)_3$. The hysteresis loop of co-precipitated hydroxides in the same ratio as in the mechanical mixture revealed uniformly porous material with a considerably lower volume of micropores in comparison to pure $Fe(OH)_3$, and a lower surface than that of the mechanical mixture. Co-precipitated specimens are more probably anomalous solid solutions not subject to the law of isomorphism. The $Mg(OH)_2$ phase was always present and $Fe(OH)_3$ was deposited in the $Mg(OH)_2$ pores and in layers of the $Mg(OH)_2$ crystal lattice, partially distorted.[8]

The mixture of Zn^{2+} and Al^{3+} oxides was employed for ^{35}S and ^{32}P decontamination from waste solutions.[9]

Hydrous oxides of tervalent metals

The tervalent metal hydroxides are still extensively studied, even though their sorption and separation properties are well known and have been reported in detail in many earlier papers.

The sorption properties of pseudomorphic iron hydroxide were studied with respect to its isoelectric point, which was found at pH 7·1–7·2.[10] Surface charge characteristics of microcrystalline particles of ferric oxide were measured in indifferent electrolyte solutions by potentiometric titration methods[11] and the surface area of iron hydroxides was determined on the basis of nitrogen and argon adsorption.[12] The sorption ability of $Fe(OH)_3$ decreases with increase in the dehydration temperature[13] and is lost on heating at 600°. Strongly sorbed cations are better separated on $Fe(OH)_3$ dehydrated at $\sim$450°, whereas less strongly sorbed cations require sorbents dehydrated at 300° or less.[14] Higher sorbability of cations occurs if the drying temperature is $\sim$125° and decreases in the order $H > Fe > Al > Pb > Ag > Cu > Zn > Cd > Mn > Ni(Co) > Ba$.[15]

The adsorption of phosphates,[13,16,17] sulphates[9] and chlorides[5] on ferric oxide in the form of sol, gel or ignited and crystalline samples was studied at different pH values. The adsorption isotherms more or less obey the Freundlich adsorption law but clear evidence of phosphate exchange for OH^- ions was not obtained.[9,16] The sorption capacity for PO_4^{3-} decreases on heating the sorbents, in correlation to the loss of H_2O from the precipitate. However, some capacity remains even after sintering at 1000°.[13] The sorption of VO_3^-, WO_4^{2-}, $Cr_2O_7^{2-}$ and MoO_4^{2-} anions was studied[18] and the adsoption mechanism, especially for MoO_4^{2-}, was examined in detail.[19] Dissolution of iron occurred during sorption of molybdate at pH 3–5.[10] The sorption of ^{131}I and ^{35}S in the form of the corresponding anions was examined and correlated with pH and electrokinetic properties of colloidal $Fe(OH)_3$ particles.[20]

For the adsorption of Cs, Na,[20] K,[12] and Ag[9] an ion-exchange mechanism was proved to be operative. The co-precipitation of nickel with $Fe(OH)_3$ was determined at different pH values[21] and in the presence of sodium and magnesium salts. A hydrolytic mechanism was observed in the absence of electrolytes but the presence of magnesium salts enabled the ion-exchange process to operate.[22] Electrolytes markedly increased the sorption capacity for nickel.[22] The adsorption of Zn^{2+}, Hg^{2+}, Mn^{2+} and Sr^{2+} ions as well as of amine complex-forming cations such as Co^{2+} and Zn^{2+} has also been presented.[17,23,24,25,26,27,46] Both hydrolytic and ion-exchange mechanisms were proved for copper adsorption.[28]

Hydrous Fe_2O_3 was successfully applied for the decontamination of waste water from ^{35}S, ^{32}P,[9,20] $^{106}Ru^{3+}$, $^{106}Ru(NO)^{2+}$,[29] $^{131}I^-$,[28,30] ^{137}Cs, ^{22}Na,[20] for Zn^{2+} isolation from rock samples,[24] and for daughter separation of ^{99}Mo–^{99m}Tc and ^{132}Te–^{132}I mixtures.[10]

A modified form of sorbent was prepared by co-precipitation of hydrated Ag_2O with $Fe(OH)_3$. The high sorption activity for ^{106}Ru, $^{106}Ru(NO)^{2+}$ and radiocobalt was examined.[29]

Hydrous alumina was also studied quite intensively, although its ion-exchange properties were known many years ago. The isoelectric points of α-Al_2O_3, α-$AlOOH$ and β-$Al(OH)_3$ are at pH 5·59, 6·78, and 6·80, respectively. The isoionic point and the point of exchange neutrality are dependent on the type and concentration of electrolyte present. The relationship between electrokinetic potential and ion-adsorption properties has been derived.[31] Dielectric loss measurements were made for single crystals of β-alumina suspended in α-alumina.[32] Adsorption of H^+ and OH^- ions at the alumina water interface and the heats of immersion of alumina in H_2O were measured. The minimum heat of immersion occurred at the equiadsorption point.[33] The rate of Na^+–H^+ exchange on hydrated Al_2O_3 decreased with increase in pH whereas the rate of Cl^-–OH^- exchange increased.[34] Irradiation of alumina ($>10^{15}$n/mm^2 γ-radiation dose of 10^7–10^9 rad) caused an increase in adsorption capacity.[35]

The dissociation of hydrated alumina occurs in the following stages: $Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^-$, $Al(OH)_2^+ \rightleftharpoons Al(OH)^{2+} + OH^-$, $Al(OH)^{2+} \rightleftharpoons Al^{3+} + OH^-$. The acid dissociation occurs according to the scheme $Al(OH)_3 \rightleftharpoons H_2AlO_3^- + H^+$.[36] The effect of pH on the ion-exchange capacity and selectivity of hydrated alumina for alkali metal cations and for univalent anions was determined at pH 4–11.[36,37,38] Saturation capacity for anions increased with decreasing pH.[36,39] Alumina showed a slight preference for Cl^- over NO_3^-,[5,36] and the affinity series $Cl > Br > I$ was established.[40] The same saturation capacity at a given pH has been shown to hold for Li^+, Na^+ and K^+. The selectivity increased in the order ($Li < Na < K$) of decreasing ionic radii of the hydrated cations. Alumina exhibits a strong preference for Cs.[36] Retention of Ca, Sr, Ba,[37,38] Zn,[23] Ni,[21] and La^{3+},[38] has been studied as a function of pH. The sorption of LiCl, $NiCl_2$, and $Cu(NO_3)_2$ was found to be partially irreversible.[38]

Applications include the following separations on hydrous alumina: Cl–Br–I,[40] ^{99}Mo–^{99m}Tc,[41] ^{35}S and ^{32}P from waste water,[9] and some thin-layer chromatographic separations.[42] Systematic study of the retention of a series of cations from $1M$ and $7M$ nitric acid and $1M$ perchloric acid by hydrous alumina has been reported with respect to possible separation applications.[43]

The use and properties of other tervalent metal hydrous oxides, such as MnOOH, $La(OH)_3$, $Sb_2O_3{\cdot}3H_2O$, $In_2O_3{\cdot}3{\cdot}5H_2O$, Ga_2O_3,[5] $Bi_2O_3{\cdot}3H_2O$[5,44] and $Cr(OH)_3$,[45] have so far been of limited interest.

Hydrous oxides of quadrivalent elements

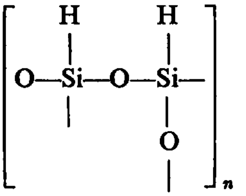
In recent years a systematic study has been made of the ion-exchange properties of quadrivalent ion oxides such as SiO_2, SnO_2, TiO_2, ThO_2, ZrO_2 and MnO_2. These oxides are usually described as hydrous oxides or hydrated hydroxy oxides and behave either as cation-exchangers in alkaline solutions or anion-exchangers in acid solutions, depending upon the basicity of the central atom and the strength of the M—O bond relative to that of the O—H bond in the hydroxyl group. Usually no sharp transition point from cation-exchange behaviour to anion-exchange behaviour exists, indicating the exchange sites to be heterogeneous. The basic ion-exchange properties of these materials have been described and reviewed earlier,[1,2,3] the recent progress in studying the exchange properties of these oxides will be reviewed in this section.

Hydrous silica

The use of silica gel as an ion-exchange substance has been extensively studied for many years.[47,48] The different types of hydrogels and xerogels are the compounds most studied, as compared with other ion-exchange materials of the oxide type.

Although the ionic adsorption mechanism on silica gel has not so far been fully established, it can be said that silica gel generally acts as a weakly acidic cation-exchanger.[49,50,51] The surface of this material is covered with OH–silanol groups, with a density of 4·6–8·0 groups per 10·0 nm,[52] ($\sim$7·8 μmole OH^-/m^2),[53] which are strong hydrogen-bond donors and may be determined by titration.[54] The conventional silica gel is an agglomeration of spheroids with diameters of the order of 10 nm, cemented by interparticle siloxane ($\equiv$Si—O—Si$\equiv$) links.[52] The aggregation is predominant near the gelation point. The aggregates, with a porous and sponge-like structure, grow to as much as 80 nm in diameter.[55] The porosity (of some hundred m^2/g) reflects this structure.[52]

A great variety in adsorption properties occurs as a result of different methods of preparation of the sorbents. Specific surfaces and porosities, which are mostly connected with the sorption activities of the sorbents, may vary widely.[56,57] High surface area silica gel was prepared by the controlled acid extraction of metal silicates and subsequent vacuum activation at 200°.[58] A soaking of preheated silica in hot hydrochloric acid was found to increase its silanol group content as well as its porosity.[59] Treating the hydrogel with higher hydrofluoric acid concentrations and subsequently aging it increases the pore volume of SiO_2 and diminishes its surface area.[60] Various geometrically modified wide-pore silica gels with low specific surface area have also been prepared by hydrothermal treatment of xerogels in an autoclave. Besides wide pores there are ultrapores accessible to H_2O but inaccessible to C_6H_6, CH_3OH and Kr molecules. Ultrapores are diminished by calcination in steam at 750°.[61] On hydrothermal treatment of hydrogels, no ultrapores were formed.[62] Modified silica sorbents with enhanced selectivity were prepared by the pretreatment of silicic acid hydrogels with various azo-dyes related to Methyl Orange, and with amines.[63,64] Silica gels with porous structure are formed by hydration of



$$\left[\begin{matrix} & H & & H & \\ & | & & | & \\ O- & Si & -O- & Si & - \\ & | & & | & \\ & & & O & \\ & & & | & \end{matrix}\right]_n$$

xerogels: $\equiv Si—H + H_2O \rightarrow \equiv Si—OH + H_2$.[65] Storage of the silicic acid xerogels makes their structure denser and decreases their adsorption activity, probably as a result of the influence of moisture.[66] Distinct cation-exchange properties with a capacity of 0·46 meq/g were obtained by treating SiO_2 with phenyltrichlorosilane in oleum.[67] Highly active silica gels were prepared by drying the wet gel (pH 7) in benzene, toluene or xylene and aging the product for 48 hr. The capacity of such a product was 2·5–3 times that of commercial silica gel.[68] On the other hand the dehydration pretreatment of silica gel by boiling with aromatic liquids leads to a decrease in capacity[69] and to deterioration of selectivity, even if surface homogenization has occurred.[70] The specific surface and porosity of silica gel are the decisive factors[71,72] influencing its sorption behaviour. For the determination of specific surface the sorption of $Zn(NH_3)_4{}^{2+}$ and $Zn(en)_3{}^{2+}$ complexes was recommended.[49] Specific surface charge density is closely connected with the surface phenomena of the sorbents. From surface charge-density measurements it was concluded that surface charge increased in the order $(C_6H_5)_4N^+ < Li^+ < Na^+ < K^+ < Cs^+$.[152] This series was in good agreement with the order of sorption affinities towards alkali metals for preparations having more than 50% of the surface area associated with pores with radii between 1·0 and 3·0 nm.[73,74]

Proton relaxation measurements of H_2O adsorbed on silica gel indicate that in most cases the proton relaxation of adsorbed liquids and gases is caused by the proton–proton dipole interaction and by the coupling between protons and paramagnetic impurities (*e.g.*, Fe^{3+}) in the sorbent.[75] The properties of adsorbed water were found to be different from those of interstitial water.[76] The molecular adsorption of H_2O on silica gel is based on hydrogen bridges formed between H_2O and hydroxylic groups on the sorbent surface.[77] The content of molecular and hydroxylic water was examined within the temperature range 100–1000° by infrared,[78] NMR,[79] and thermogravimetric methods. EPR measurements show the loss of the surface hydroxyl functional groups and the formation of $\equiv SiO^-$ radicals after γ-irradiation of SiO_2.[80]

The changes occurring in silica gel on thermal treatment have been widely examined. The adsorption ability of sorbents gradually decreases as they are heated to 100–300°, but in the temperature range 300–1000° substantially increases, *e.g.*, for Rb^+.[81] This increase is explained by the conversion of the original compound of $\equiv\mathrm{Si}\begin{smallmatrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH^-}\cdots\mathrm{H_3O^+}\end{smallmatrix}$ by calcination at over 500°, probably to $=\mathrm{Si}\begin{smallmatrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH}\end{smallmatrix}$ and $-Si(OH)_3$ compounds, which have higher capacities.[81] Great changes in the physical properties of the sorbent are caused by hydrothermal treatment[82,83] up to 1050°. Thus the surface area decreased from 580 to 25 m^2/g, mean particle size increased from 5 to 105 nm, and mean total pore volume increased from 0·74 to 2·31 ml/g.[83] On heating of silica gel at 200–400° in vacuum, the density of surface OH^- groups was lowered to a minimum value of 3·5 μmole OH^-/m^2, but at temperatures $>400°$ the destruction process was substantially retarded.[53] On the other hand the presence of Na^+ in the gel enhanced the calcination effect.[84] The degree of hydration can be determined by the interaction of $TiCl_4$ with the OH^- groups of SiO_2.[85] The solubility and the dissolution kinetics of precipitated amorphous silica in 1*M* $NaClO_4$ have been discussed.[86]

The adsorption mechanism of non-hydrolysing cations on silica gel is mostly interpreted in terms of ion-exchange:[71,87–90] $m(\equiv SiOH) + M^{n+} \rightleftharpoons [(\equiv SiO)_mM]^{m-n} + mH^+$ ($m = n$ for all systems examined).[87] There are some suggestions that besides this mechanism physical adsorption and ion exclusion from small pores may also occur even for alkali metal ions.[73] These conclusions, however, conflict with the results of other authors, where only ion-exchange is postulated, especially for alkali metals.[74] Special attention is paid to $Al(OH)_3$ impurities in the crystal lattice of SiO_2. In contradiction to earlier papers, the sorption process at pH $<8{\cdot}0$ is said to be unaffected by the presence of $Al(OH)_3$ in the sorbent.[91] Adsorbed cations are weakly bound to the surface sites of silica gel and are readily exchangeable.[52] Affinity for the surface is governed by the electron density distribution in the surface area and between $\equiv SiO^- \cdots M^{n+}$ bonds.[93] Generally, the affinity increases, going from univalent to tervalent elements.[51,94] For elements of the same charge, the adsorption is enhanced by decrease in the crystallographic diameter, *e.g.*, RbOH < KOH < NaOH < LiOH, $Ba^{2+} \sim Sr^{2+} < Mg^{2+} < Be^{2+}$, and $In^{3+} < Ga^{3+} < Al^{3+}$.[91,94,95] However, these affinity series may be dependent upon the type of the sorbent used or on the experimental conditions applied. There are great differences in the results presented, especially for univalent and bivalent cations, and quite opposite affinity series have been found.[73,91,94,96] The mechanism of ion-exchange is supported by the shift of the infrared vibration of the $\equiv SiO^- \cdots M^{n+}$ bond. The adsorbability of the transition metal ions on the Ca form of silica gel increases as their charge increases. The limiting value for the uptake of M^{3+} ions is 3·2–4·5 meq/g and of M^{2+} ions 1·8–2·5 meq/g. There is a steady increase in the adsorption of tervalent ions with an unfilled *f*-shell, in the order La < Ce < Nd < Gd < Tb < Y < Er < Tm < Yb < Lu < Sc, *i.e.*, with decrease in their ionic radius.[93] The results are in agreement with the idea of the possible contribution of covalent bonding as well as of electrostatic forces to the energy of the adsorption bond Si—OM. Labile co-ordination complexes, *e.g.*, *trans*-$Co(en)_2Cl_2^+$, are also adsorbed by SiO_2. Adsorbed inert complex cations which contain an aquo ligand react with surface silanol groups to bind $\equiv SiO^-$ in the co-ordination sphere, and in media of low dielectric constant $\equiv SiO^-$ can directly displace Cl^- in the absorbed *trans*-$Co(en)_2Cl_2^+$.[52]

The values of specific surface area as well as the pore diameter are decisive for the kinetics of exchange reactions. The rate of exchange in the case of colloidal silica was governed by both film and particle diffusion mechanisms. Preheated silica samples give a fast uptake process followed by a slow one. The first process is mainly chemically controlled, the second is governed by chemical reaction as well as by particle diffusion.[59]

Of the univalent cations, the sorption of alkali metals has been mostly studied.[57,73,74,81,90,94,95,97] Alkali metal dichromates react reversibly with the surface of silica gel. The reaction has been shown to occur either by adsorption or by equivalent exchange of cation and anion.[98] The adsorption of Ag^+ increases with increasing pH with a high uptake of 7·96 mmole per mole of SiO_2 at pH 7·86.[99] The Ag^+ adsorbed on SiO_2 is reduced to metallic Ag, as proved by EPR measurements.[157]

The sorption of bivalent cations on different SiO_2 preparations has been examined.[49,90,94,100,101,102] Ionic forms of hydrogels and the structure of the globules of polysilicic acid xerogels have been studied with respect to different forms of the sorbents (Ca^{2+}, Na^+, Li^+, and H^+) and to the sorption properties of bivalent and tervalent cations at pH 3.[103] Silica gel in the Mg form exhibits the following sorption affinity series: Cu > Ni > Zn > Mg.[104] The adsorption of *tris*-phenanthroline complexes with Zn^{2+}, Cu^{2+}, and Fe^{2+} was found to occur as a pure ion-exchange process.[105] Ion-exchange adsorption of $Zn(NH_3)_4^{2+}$ and $Zn(en)_3^{2+}$ complexes is independent of pH in the pH interval 6·00–9·20 and on the surface areas from 50 to 500 m^2/g.[49] The H^+–Cu^{2+} exchange[57,72] is strongly dependent on pH, specific surface and pore diameter of silica gel. Only 60% of the OH groups can react with the Cu^{2+} ion and the compound $0{\cdot}6$–$0{\cdot}9CuO{\cdot}SiO_2{\cdot}nH_2O$ is formed. In all the ion-exchange stages molecular sorption on the SiO_2 surface and skeleton occurs. Narrow-pore samples can adsorb Cu^{2+} ions less than can wide-pore silica; after Cu desorption the skeleton is capable of adsorbing more water molecules than it could originally. The electron reflectance and ESR spectra of a series of Cu^{2+}, Ni^{2+} and Co^{2+} complex cations with multidentate nitrogen ligands adsorbed on SiO_2 gel were examined and discussed in terms of adsorption mechanism.[153–156] The EPR method was applied to the study of Mn^{2+} ions adsorbed on silica gel sorbents.[106]

The adsorption of tervalent cations such as Al, Ga, In, Tl, Bi, Fe, and Cr has been studied over a wide range of pH and silica gel products.[90,94,97,103] The extent of adsorption of Al^{3+} from an acetate buffer by coarsely porous silica gel does not exceed significantly the number of the hydroxy groups present on the surface of the sorbent.

During the adsorption the sorbents depolymerize. The quality of the dissolved silicic acid is improved in proportion to how much Al^{3+} goes over into the composition of the solid phase.[107] For the adsorption of $FeCl_3$, $AlCl_3$, and $CaCl_2$ from $SnCl_4$ media, the differential adsorption heats were found to be 31·2, 47·7 and 23·8 kJ/mole, respectively.[101,108]

The adsorption of multivalent cations such as Pa, Zr, Nb, Ac, Th, U, from concentrated acid solutions has been studied.[51,59,100,109,110] The most favourable pH for Th adsorption was 2·5–2·9 and the adsorption process was irreversible.[111] Special attention was paid to Zr adsorption. The adsorption process and elution rate are highly dependent on the acidity of the original solution and the kind of anion.[51,112] Zr and Hf are probably hydrolysed after diffusion into the silica gel phase.[113] The break-through capacity corresponds to 0·6–0·7 mg atoms of Zr per g of SiO_2.[114] Zirconium adsorption is substantially increased in the presence of phosphoric acid, which is explained in terms of molecular adsorption of neutral phosphate complexes of Zr.[115]

The adsorption mechanism of hydrolysed cations on SiO_2 is very complicated and only qualitative conclusions are drawn from the experimental results. Besides the ion-exchange process, surface adsorption phenomena are supposed to occur with many hydrolysates,[71,88] *e.g.*, the adsorption of heavy metal ions on silica gel from solutions of high pH is treated as occurring in two stages: (1) ion-exchange of the acid H^+ on silica gel for a heavy metal ion; (2) establishment of adsorption equilibria for molecular adsorption of a slightly soluble metal silicate on the silica gel network. The law of mass action is then applied.[116] Hydroxides react with SiO_2, forming the following anions: $\equiv SiO^-$, $\left[\begin{array}{l}\equiv Si{-}O\\ \qquad\ \ |\\ \equiv Si{-}OH\end{array}\right]^-$, and $\left[\equiv Si\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}\right]^-$.[52] The adsorption of $Ca(OH)_2$ on different silica gels with specific surfaces areas ranging from 51 to 693 m^2/g proceeds in two stages. The fast adsorption stage is connected with an ion-exchange process, the subsequent slow one with the formation of a new, $CaSiO_3$, phase.[117] The adsorption of hydrolytic products of Co, Mn, Cu, Ni and Zn tracers was found to increase with increase in pH. These hydroxo-complexes are adsorbed by an ion-exchange mechanism, except for Cu.[118] The same adsorption increase with pH was observed for Th^{4+}, Fe^{3+}, Al^{3+} and Cr^{3+} hydrolysates. Thorium was adsorbed as $[Th(OH)]^{3+}$ and $[Th(OH)_2]^{2+}$, and as $[Th(CH_3COO)_3]^+$, $[Th(OH)(CH_3COO)_2]^+$, and $[Th(OH)_2(CH_3COO)]^+$ from acetate buffers. Other hydrolytic complexes were adsorbed in the forms of $[Al(OH)(H_2O)_5]^{2+}$, $[Al(CH_3COO)(H_2O)_5]^{2+}$, $[Fe(CH_3COO)]^{2+}$ $[Fe(CH_3COO)_2]^+$, $[Fe(OH)(CH_3COO)]^+$, $[Cr(H_2O)_6]^{3+}$, $[Cr(OH)_6]^{3-}$ and $[Fe(CH_3COO)_3]$.[119,120] Zirconium hydroxo-complexes were found to be adsorbed even from highly concentrated nitric acid solutions.[112] The cationic and neutral hydroxo-complexes of Zr and Hf are supposed to be adsorbed by molecular adsorption.[113] In the case of protactinium the neutral or anionic hydroxo-complexes are quickly adsorbed over the acidity range 4–10*M* hydrochloric acid; at higher acidities the adsorption of $H_{(x-5)}PaCl_x$ is supposed to occur. The sorption of neutral bisulphate complexes was established for the concentration range 3–7*M* sulphuric acid. The cationic hydroxo-complexes are adsorbed much more slowly. The adsorption process for the compounds mentioned above has features of molecular adsorption.[110] Adsorption of Pa from hydrochloric and sulphuric acid media follows the Freundlich adsorption isotherm and decreases with increasing acidity.[121] The adsorption of Nb and Ta hydrolysates from hydrochloric, nitric, sulphuric and perchloric acid solutions onto hydrous and silicon-treated SiO_2 was observed. Lower adsorption occurred on silicon-treated sorbents. Mixed neutral complexes of niobium, $Ta(OH)_5$ and $Ta(OH)_mCl_{(5-m)}$ are supposed to be adsorbed.[122,123]

The sorption of different cations on silica gel from organic and mixed aqueous–organic media has also been studied. LiCl, $LiNO_3$ and NaI, dissolved in acetone, react reversibly with the sorbent without ion-exchange. The extent of reaction is enhanced by the addition of small amounts of water.[124] The mixed aqueous–organic solutions have the following important effects on the adsorption: solvation and complex formation, salting-out of the complexes from the liquid into SiO_2, and selective uptake of the solvents. The partition of Zr, Hf, Nb and Ta between SiO_2 and 1–10*M* hydrochloric acid in the presence of 0–90% v/v of methanol, ethanol, isopropanol, acetone and dioxan in water was determined.[125] The adsorption of Zr and Hf was increased with increase in the amount of organic component. At higher alcohol content in acid solutions no sorption occurred of the elements of groups I, II, and III and of U^{6+}, Fe, Al and Th.[114] On the other hand, a sudden drop of Nb adsorption was achieved in the presence of dioxan,[126] and a gradual decrease in adsorption of Pa and of the reaction rate was found with increase in the organic component concentration.[127,128]

Many papers deal with the use of silica gel for the separation of individual elements or groups of elements in different combinations. The following separations have been described: Na–Rb–Cs–Fr.[96,129] Tl–Bi;[97] LiCl, $LiNO_3$, NaI—isolation from acetone;[124] Cs–Hf;[114] Cs from waste water;[130,131] Sr from waste water;[92,130] Co–Ni;[87] Co–Cu, Zn, Ni, Tl;[132] Cu from waste water;[133] $Cu–Cr^{6+}$;[134] Zn—determination in Cu;[87] Zn–Cu, Ag, Ni, Cd, Co, Fe, Mn, W;[102] Al–Fe;[87,120] Fe, Al–Sr, Cu, Zn, Co, Ni, Mn;[120] Eu–Zr–Hf;[135] Ce from waste water;[130] Bi–Pd, Tb;[97] Zr–Nb;[126] Zr, Nb–Sr, Ce, Ru, Al;[136] Zr–K, Na, Ca, Mg, Zn, Mn, La, Al, Fe, Ti, Th;[137] Zr–Hf on the macro-scale;[138] Zr–Cs, Sr, Eu;[114] Zr, Hf–La, U^{6+}, Fe, Al;[114] Zr, Hf–alkali metals, alkaline earth metals, rare earth elements, Al, Fe, Th, U^{6+};[135] Zr–Pa–Hf–Nb;[128] Zr–minerals;[51] Zr–bulk concentration of Th;[139] Nb–Ta;[123] Hf–Eu;[114] Pa–U ores;[128] Pa–irradiated Th;[100,128,140,141] Pa–U;[141] $Pa^{4+}–Pa^{5+}$;[142] U–Pu–fission products;[143,144] Cr^{6+}–Cu, Ni, Zn, Cd;[134] Sr–Hf;[114] Fe^{2+}–Cu, Hg, Cd, Zn, Ni, Bi;[87] Co^{2+}–Cu, Hg, Cd, Zn, Bi.[87]

Thin-layer chromatography[42,71] has also been applied for studying the adsorption of Li, Na, K, Rb, Cs, Ca, Sr, Ba, Al, Zn, Cd and Hg^{2+} cations on SiO_2,[88,145] for mutual separation of phosphate, pyrophosphate, phosphite and hypophosphite,[146] and for Sr–Y, Ba–La and Ba–Cs[147] separations.

Special attention has been paid to those sorbents of which silica gel is one of the main structural components. Acid treatment of silicic acid gels co-precipitated with various metal hydroxides, such as $Fe(OH)_3$, $Pb(OH)_2$, $Co(OH)_2$, $Cr(OH)_3$ and $Mg(OH)_2$, gives samples of silica gels with essentially different porosity types. Mild acid treatment with diluted acids at room temperature retains a porous type of co-precipitate gel in the product. A more vigorous acid treatment at boiling point yields silica gels of mixed porosity.[148] Silica–alumina sorbents with the Al/Si ratio of 1/3 have cation-exchange properties.[149] The rates of exchange[150] as well as the adsorption isotherms for $H^+–NH_4^+$ and $H^+–Mg^{2+}$ ion-exchange[149] were studied with this sorbent. The protonic sites on the silica–alumina solid can form 2- or 3-co-ordinate bonds on the surface. The strongly protonic acid sites disappear when the product is calcined at 1000°. The weak, remaining protonic acid sites exchange only at pH > 8 with univalent cations such as NH_4^+.[151]

Stannic oxide

Hydrous stannic oxide is prepared by the acidification of sodium stannate solution or by the reaction of nitric acid with tin metal.[158] By the former procedure α-stannic acid is formed, and β-stannic acid by the latter. The products are stable towards highly concentrated nitric and sulphuric acid solutions.[158]

X-Ray, DTA and Mössbauer spectra measurements[158] suggest that the exchanger is "wet" SnO_2 and that SnO_2 is simply a host for adsorbed water, which itself must act as the exchanger.[158] Thus it may be formulated as $SnO_2 \cdot xH_2O$.

Hydrous stannic oxide behaves both as cation- and anion-exchanger,[158,159] especially selective for bivalent transition metal and uranyl ions. It is interesting that the selectivity series[158] $Cu > Zn > Co \geqslant Fe(II) > Ni > Mn$ closely parallels the order of the equilibrium constants of the hydrolytic reaction $M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+$. Alkaline earth metal cations are weakly adsorbed[160] whereas tervalent metal ions such as Al^{3+} and Cr^{3+} are strongly adsorbed. A co-precipitation rather than an ion-exchange mechanism is suggested for the adsorption of the latter ions.[158] The selectivity series $PO_4^{3-} > C_2O_4^{2-} > SO_4^{2-} > Cr_2O_7^{2-} > Fe(CN)_6^{4-} > Fe(CN)_6^{3-} > Cl^- > MnO_4^- > Br^- > I^-$ has been reported[159] for the exchange of anions.

Hydrous stannic oxide is suitable for column separation of bivalent transition metal ions (Cu–Zn, Cu–Co, Cu–Fe, Cu–Ni, Cu–Mn, Mn–Zn, Mn–Ca, Co^{2+}–Fe^{3+}).[160] Separations of W(VI) from solutions containing Mo(VI) and Fe(III)[161] and the removal of UO_2^{2+} and transition metal ion contamination from aqueous solutions have been described.[159] The exchanger, in NH_4^+ from, is suitable for alkali metal and alkaline earth separations.[159] High selectivity for Cu^{2+} ions enables their separation to be made by co-precipitation with hydrous stannic oxide.[162] The anion-exchange behaviour of hydrous stannic oxide has been used for the separation of $Cr_2O_7^{2-}$–MnO_4^-.[159]

Titanium oxide

Hydrous titanium oxide is prepared by mixing titanyl oxalate or $TiCl_4$ solutions with sodium hydroxide.[163,164] The precipitates obtained are usually dried at room temperature[163] or at 400°.[163,165] White amorphous products are obtained which lose free or interstitial water up to 200° and chemically bound water at higher temperatures (200–500°). The amount of chemically bound water is very low (1–2%).[164] Infrared measurements[164,166] indicate the presence of H_2O molecules more or less bonded to the solid and also of OH groups bonded to the metal atom. Similar measurements made on analogous hydrous oxides of Zr, Hf and Th[166] have shown that the number of OH groups bonded to the metal atom is the lowest for Ti and the highest for Th. Further, a correspondence has been found between the infrared Ti–O absorption band (and also of Zr–O, Hf–O and Th–O bands) of the hydrous oxide and that in the crystal oxide after thermal treatment. Hydrous titanium oxide is thus formulated as a hydrated hydroxide oxide of a general formula $TiO_{(2-x)}(OH)_{2x} \cdot yH_2O$,[166–168] with x probably <1 However, the formula $TiO(OH)_2 \cdot nH_2O$ has also been proposed.[164]

Hydrous titanium oxide is insoluble in acid as well as in alkaline solutions.[163] The exchanger is very suitable for use in column operations and can be easily regenerated for reuse.[163]

Titration curves of this exchanger exhibit three characteristic points indicating the polyfunctional character of the exchanger.[169,170] There are three protons exchangeable for every 10 Ti atoms.[169,170] The constants for the successive dissociation of the three protons were determined.[169]

The exchange capacity of hydrous titanium oxide is dependent on pH, ranging from ~2·0 meq/g at pH ~12·5 for Ca^{2+} and Sr^{2+} to ~1·5 meq/g at pH ~4 for Co^{2+}, Ni^{2+} and Cu^{2+}.[164] Samples heated up to 400° still show a high exchange capacity.[164] Distribution coefficients for the exchange of Na^+, Rb^+, Cs^+, Sr^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Cr^{3+} have been determined.[164] The affinity series $Na < Rb < Cs$ has been found for alkali metal ions; the affinity series of transition metal ions coincides with the stability order of the respective complexes, *i.e.*, $Cu > Ni > Co$. The plots of $\log K_d$ *vs.* $\log [H^+]$ are linear for the exchange of univalent and bivalent cations, with slopes corresponding to the valency of the ion exchanged.[164] However, species such as $SrOH^+$ are adsorbed in the case of Sr^{2+}. In alkaline solutions the adsorption of Sr^{2+} led to the formation of a crystalline compound with a 1:1 Sr:Ti ratio.[169] Such behaviour was not observed for the sorption of alkali metal cations.[169] High adsorption of Fe^{3+} was ascribed to the formation of a stable chemisorption bond between the hydrated oxides of Ti and Fe.[171]

Thermodynamic equilibrium constants of the Cs^+–H^+ and Na^+–H^+ exchange[169,172] have been determined from the adsorption isotherms for the three exchange stages (Cs^+–H^+: $10^{-3\cdot29}$, $10^{-5\cdot47}$, $10^{-7\cdot60}$, Na^+–H^+: $10^{-3\cdot81}$, $10^{-6\cdot28}$, —). For the Tl^+–H^+ exchange, six exchange stages have been found with the following constants: $10^{-0\cdot52}$, $10^{-1\cdot97}$, $10^{-3\cdot42}$, $10^{-4\cdot87}$, $10^{-6\cdot32}$, $10^{-7\cdot77}$.[173]

Kinetic measurements on the Cu^{2+}–H^+ exchange[163] indicate that the rate of exchange is diffusion controlled, with the diffusion coefficient of ~2·5 . 10^{-4}mm^2/min and activation energy of 20·3 kJ/mole.

High chemical and radiation stability as well as good mechanical properties of hydrous titanium oxide permitted its application for the removal of Pu and certain fission products (Ru, Zr, Nb) from alkaline (Na_2CO_3) media[174] or from highly radioactive solutions[175] as well as for concentrating uranium from sea-water.[176] The use of papers impregnated with hydrous TiO_2 has been reported for the separation of U,Ni,Co,Cu and Fe(III).[177] Hydrous titanium oxide has been also described as a co-precipitating agent for small amounts of In^{3+}, SeO_2^{2-}, PO_4^{3-} and Cu^{2+}.[162,178,179,180]

Thorium oxide

Hydrous thorium oxide is usually prepared by mixing thorium nitrate solution with alkalis in various initial ratios of the reactants.[163] White, glassy-looking, amorphous products are obtained, which lose free or interstitial water on heating up to 200° and bonded water up to 500°.[164] The results of thermogravimetric (TGA), DTA, X-ray and infrared analyses suggest that the samples dried at room temperature contain Th-O and OH groups as well as H_2O molecules and that the general formula may be written as $ThO(OH)_n \, . \, nH_2O$.[164] On heating of the exchanger *n* decreases owing to the water loss, which is accompanied by a decrease in surface area.[164] The formation of cubic ThO_2 was observed on heating to over 300°.[181]

Hydrous thorium oxide behaves both as cation- and anion-exchanger. Relatively high capacities for Ca^{2+} and Sr^{2+} ions have been found at pH $\sim 12(\sim 2{\cdot}0$ meq/g), which decreased substantially with decreasing pH. An anion-exchange capacity of $\sim$1 meq/g has been reported for acid solutions.[163] The distribution coefficients determined for Na^+, Rb^+, Cs^+, Sr^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+} and Cr^{3+} show a regular selectivity series for alkali metal cations ($Cs > Rb > Na$). The selectivity series of transition metal ions ($Cu > Ni > Co$) coincides with the stability order of the respective hydroxo-complexes,[164] similarly to the behaviour of hydrous Sn and Ti oxides.[158,164]

Kinetic measurements have been made for the Cu^{2+} and Sr^{2+} exchange.[163] The Bt *vs.* t plots are linear[163] indicating a diffusion-controlled exchange process ($B = \pi^2 D/r^2$, where D is the effective diffusion coefficient of ions within the exchanger and r is the radius of the exchanger spherical particles; t = time). The reaction rate is very slow in comparison with other hydrous oxides.[163] The diffusion coefficient for the Cu^{2+} exchange ($2{\cdot}2 \times 10^{-5}$ mm^2/min) and activation energy (about 71 kJ/mole) have been estimated.[163]

It is interesting that heated ThO_2 possesses adsorption ability towards phosphates, the process being very probably solution diffusion-controlled with an activation energy of 12·5 kJ/mole.[182] The formation of thorium phosphate was found to occur on co-precipitation of phosphates with hydrous thorium oxide.[180]

Hydrous thorium oxide in mixture with other inorganic ion-exchangers has found good application in inorganic ion-exchange membranes. Thus membranes made from hydrous ThO_2 and CeO_2 are stable at high temperatures, are unaffected by corrosive and oxidizing agents and can be used for demineralization of saline water.[183] Similarly, combined anion/cation-exchange membrane systems consisting of ThO_2 and zirconium phosphate[184,185] or ThO_2 mixed with other oxides, and zirconium phosphate membranes have been reported for the same purpose.[186]

Zirconium oxide

Hydrous zirconium oxide is usually prepared by mixing zirconium salt solutions with alkalis. Well granulated materials are obtained by freeze-drying the gels at 268, 263 and 258 K.[187] This procedure does not affect the ion-exchange capacity and is suitable also for the preparation of other granular hydrous oxides.[187] An exchanger of suitable mechanical properties has also been prepared as a mixed hydrous ZrO_2–hydrous SiO_2 gel.[188]

Although the structure of amorphous hydrous zirconium oxide has not yet been properly resolved, a tetrameric structure is suggested, based on the known tetrameric species in hydrolysed Zr(IV) salt solutions, for the freshly prepared zirconium hydroxide—$[Zr(OH)_4]_4$. On aging, the $[ZrO(OH)_2]_4$ structure is formed.[189] The evidence for the presence of hydroxyl groups was found by Clearfield.[190] X-Ray data on crystalline zirconium hydroxide suggest a structure which is analogous to ZrO_2, *i.e.*, $[ZrO_2]_n$, with H_2O and OH groups.[191]

Hydrous zirconium oxide behaves both as cation- and anion-exchanger[192,193] with the zero-point of charge at pH 6·05.[194] Thermodynamic equilibrium constants of ion-exchange reactions of some alkali metal cations[195] and some anions[196,197] have been determined by Nancollas *et al.* and are summarized together with the corresponding thermodynamic quantities in Table I.

TABLE I.—THERMODYNAMIC QUANTITIES FOR ION-EXCHANGE ON HYDROUS ZrO_2[195–197]

System	*K*	$\Delta G°$ *kJ/mole*	$\Delta H°$ *kJ/mole*	$\Delta S°$ *J/mole/K*
Li^+–K^+	40·2	−3·4	1·0	15
Na^+–K^+	1 52	−1·0	0·3	5
Cl^-–NO_3^-	1·04	−0·6	4·1	16
SCN^-–NO_3^-	1·94	−1·6	−7·8	3
SCN^-–Cl^-	1·54	−1·2	−4·8	−13

The thermodynamic equilibrium constants for alkali metal cations show an unusual affinity series, Li > Na > K,[195] in contradiction to the earlier reported affinity series.[1] It has been found[195] that all the Li^+, Na^+ or K^+ forms of the exchanger contain the same percentual amount of water and it has been concluded that the ingoing ions should be substantially dehydrated within the exchanger. Thus the positive entropy changes, accompanying the release of H_2O molecules from the co-ordination spheres of ingoing ions may be responsible for this unusual affinity series. The equilibrium constants for the exchange of anions show a slightly higher selectivity towards chloride as compared with nitrate,[197] which is ascribed to an entropy effect, when the entropy change is sufficient to overcome the unfavourable endothermic enthalpy change. The exchange of SCN^- anions is exothermic, which probably reflects some covalency in the bonding between the exchanger matrix and SCN^- ion.[197]

In addition to the anions mentioned above, it is well known[1] that hydrous zirconium oxide is highly selective towards phosphate ions, even at high temperatures and pressures.[198] The adsorption of phosphates was found even on heated ZrO_2[199] as well as on heated ThO_2, HfO_2, CeO_2 and Zr powder.[200] A fixed stoichiometry between the adsorbed phosphates and the surface sites of the metal oxide has been found.[199]

Hydrous zirconium oxide has recently become important in the water desalination process by hyperfiltration. Dynamically formed membranes made from this material show promising salt-rejections by virtue of Donnan electrolyte exclusion.[201,202,203] Other applications such as quantitative mutual separation of I^-, Br^- and Cl^-[204] as well as a series of separation processes using co-precipitation of Pu,[205] Sc, Ti, V,[206] Mo, W,[207] Zn,[208] In^{3+},[178] and SeO_2^{2-},[179] with hydrous zirconium oxide have been described. Hydrous zirconium oxide, in mixture with hydrous alumina, is suitable for the determination of traces of V in Al matrices by neutron-activation analysis.[209] By treatment of the hydrous ZrO_2 with dithionite, phosphite, sulphide, thiosulphate, dichromate, permanganate and oxalate solutions, electron-exchanging ion-exchangers are obtained.[210]

Manganese dioxide

Hydrous manganese dioxide is prepared by mixing $KMnO_4$ and $MnSO_4$ solutions at 90°,[211] or by electrodeposition from a solution of $MnSO_4$ at ~100°.[212] Depending on the method of preparation and the drying temperature, different products are formed with structures close to β-, γ-, or ρ-MnO_2.[1,211,212] Non-stoichiometric composition has often been found (for example $MnO_{1.88}$[211]) which can be expressed by an empirical formula $(MnO_x)_2OH$,[213] where $x = 1{\cdot}70$–$1{\cdot}75$. It is supposed that the OH groups which are distributed through the whole volume of hydrous manganese dioxide differ in their acid-base properties.[213] Their pK values have been determined at an ionic strength of $0{\cdot}1M$(pK_1 = 3·6, pK_2 = 5·5 and pK_3 = 9·3).[213] The corresponding total capacity is 0·5 meq/g and decreases on heating of the exchanger.[213,214] This maximum capacity value indicates that there is one exchangeable OH group per two MnO_2 molecules, in accordance with the above-mentioned empirical formula.[213]

Hydrous manganese dioxide is more selective towards alkaline earth metal cations than alkali metal cations;[214] pyrolusite and γ-MnO_2 exhibit high adsorption capacity for NH_4^+ and Zn^{2+},[215] and bivalent transition metal ions.[216]

The adsorption mechanism on hydrous manganese dioxide seems to be rather complicated. An ion-exchange mechanism is reported for the adsorption of alkali metal ions on $(MnO_x)_2OH$[214] and for Ag^+, Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+} and Nd^{3+} on colloidal manganese dioxide.[217,218] However, in the case of alkaline earth metal cations the adsorption of MCl^+ and at higher concentrations the molecular sorption of MCl_2 species has been observed.[214] In addition to the ion-exchange process, some other kinds of retention may occur. Thus chemical reaction of Cr^{3+} or Mn^{2+} ions with MnO_2,[211,219] formation of a colloidal suspension in the case of Fe^{3+} adsorption[211] or a redox process yielding insoluble products in the case of WO_4^{2-}, MoO_4^{2-} and AsO_4^{3-},[220] have been reported as factors causing some irregularities when these processes are treated as pure ion-exchange.

The isotherms for the Ba^{2+} and Mn^{2+} adsorption on β-MnO_2[219] and for Eu^{3+}, Tb^{3+}, Sc^{3+}, Mn^{2+} and Cr^{3+} on ρ-MnO_2[211] have been determined. For the latter, the isotherms (with the exception of that for Cr^{3+}) fit the Langmuir adsorption equation. Large differences in the adsorption capacities between the individual ions could be explained only by the Langmuir model and it was assumed that the number of adsorbing sites in MnO_2 was not the same for different ions, which, depending upon their size, could be more or less well accommodated in the irregular structure of the MnO_2 particles.[211]

A series of useful separations[43] on hydrous manganese dioxide have been described: ^{51}Cr retention and ^{60}Co–^{59}Fe separation for the neutron-activation analysis of Fe–Cr alloys;[211] carrier-free parent–daughter separations (^{49}Ca–^{49}Sc, ^{90}Sr–^{90}Y, ^{32}S–^{32}P);[211] separation of ^{140}Ba and ^{140}La from Ce,Zr and Nb;[211]; mutual separation of Na, K and Cs;[220]; separation of Tc from Mo for obtaining carrier-free ^{99m}Tc of high purity;[221] separation of Ra from liquid wastes.[222] Hydrous MnO_2 in mixture with hydrous Fe_2O_3 is suitable as a scavenger for ^{60}Co, ^{106}Ru and ^{65}Zn from sea water[223] or for the removal of various radionuclides from aqueous solutions.[224]

Hydrous oxides of quinquevalent and sexivalent metals

Hydrous oxides of Sb, V, Ta, Nb, Mo(VI) and W(VI) have been described as ion-exchanging materials. Among them hydrous antimony oxide (so-called antimonic or polyantimonic acid) has been the most intensively studied, owing to its considerable adsorption capacity and a reasonable rate of adsorption and desorption when used in column operations.

Antimonic acid

Various antimonic acid materials have been obtained with different chemical composition and ion-exchange properties, depending on the method of their preparation as well as on aging. The species can be divided into three groups —crystalline, amorphous and glassy.

The well defined *crystalline antimonic acid* is prepared by the hydrolysis of $SbCl_5$ with a large amount of water and aging of the gel in the mother liquor at 30° for 20 days.[225] The time of aging can be reduced by increasing the temperature to 80°,[226] or to 130–180°.[227] The other methods of preparation are based on passing an aqueous $KSb(OH)_6$ solution through a column filled with Dowex 50 or KU-2[227] followed by subsequent evaporation[228] or treating the effluent with nitric acid. Good sorbents were obtained by thermal polymerization of $NaSb(OH)_6$ at 250° and subsequent treatment with nitric acid.[229] The chemical composition of the crystalline antimonic acid corresponds to the empirical formula $Sb_2O_5{\cdot}4H_2O$[226,227,229,230] for samples dried at up to 50° and $Sb_2O_5{\cdot}3\text{–}4H_2O$ for species obtained after drying at 70–90°.[228] The acid is practically insoluble in water and 4*M* hydrochloric acid.[228]

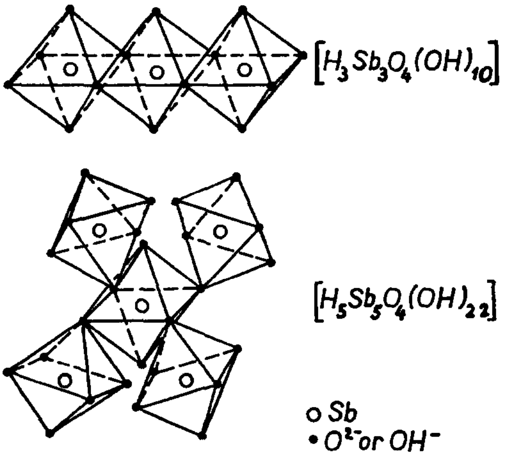
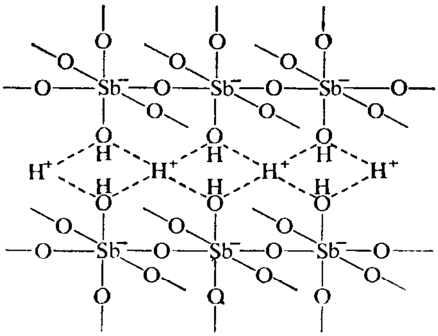


FIG. 1.—Tentative structure of crystalline polyantimonic acid.[230]

Contradictory statements have been reported for the structure of antimonic acid. X-Ray diffraction measurements lead to a cubic structure with an *a* parameter of 1·025,[230] 1·038[225] and 1·029 nm.[227] Baetslé and Huys,[230] on the basis of the empirical formula $Sb_2O_5{\cdot}4H_2O$, the density of 4·27 and the lattice parameter $a = 1{\cdot}03$ nm, deduced that the molecular weight was about 2800, implying 14 Sb atoms per unit cell. The structure proposed is built up of trimeric units [empirical formula $H_3Sb_3O_4(OH)_{10}$] with 4 oxygen atoms common to 3 Sb atoms, and a pentameric unit [empirical formula $H_5Sb_5O_4(OH)_{22}$] with 4 oxygen atoms of the central Sb octahedron linking four $Sb(OH)_6^-$ groups around it. Both structures are shown in Fig. 1. Three trimeric units and one pentameric form one unit cell of an empirical formula of $\{[H_3Sb_3O_5(OH)_8]_3\}[H_5Sb_5O_6(OH)_{18}]$. This empirical formula takes into account the interconnecting oxygen atoms which link the trimers to each other, as well as the trimers to the pentamer.[230] The fourteen hydrogen atoms are supposed to be exchangeable, corresponding to the theoretical exchange capacity of 5·05 meq/g. Capacities very close to this value have been found for Ag^+, Tl^+, Pb^{2+} and Sr^{2+}.[227,230,231]

Infrared measurements by Abe and Ito[225] led to the following structure with an empirical formula of $H_2Sb_2O_5(OH)_2$:



The hydrogen ions in the structure may be combined with H_2O molecules as H_3O^+ ions. It is supposed[225] that the hydrogen-bonding surface groups are constrained by rigid three-dimensional bonding and that the exchangeable hydrogen ions are surrounded by six oxygen atoms, as is Na^+ in $Na[Sb(OH)_6]$.* The presence of Sb–OH groups is confirmed by the occurrence of the infrared absorption band at 1280 cm^{-1} and that of the hydrogen bonds by a broad band at 2700–3800 cm^{-1}.[225] On the other hand, Novikov *et al.*[227,232] postulated the compound $H_3OSbO_3 \cdot 0 \cdot 48H_2O$ with molecules of adsorbed water. These authors support this conclusion by the isomorphism of antimonic acid with $AgSbO_3$ and a cubic $NaSbO_3$ as well as by infrared measurements.

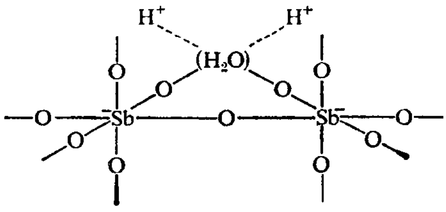
TGA, DTA and X-ray studies[233] of thermal decomposition of the crystalline antimonic acid show a reversible loss of 2 molecules of water up to 200° with formation of crystalline $Sb_2O_5 \cdot 2H_2O$ without change in the adsorption capacity. On further heating the loss of bonded water occurs with stepwise formation of Sb_2O_5, Sb_6O_{13} and Sb_2O_4. Another scheme of thermal decomposition, leading to the stepwise formation of H_3OSbO_3, Sb_3O_6OH, Sb_6O_{13} and Sb_2O_4, has been proposed by Novikov *et al.*[227]

Amorphous forms of antimonic acid ($Sb_2O_5 \cdot nH_2O$) are prepared by hydrolysis of $SbCl_5$ and aging of the gel in the mother liquor for 4 hr,[226] by hydrolysis at low temperature,[234] or by low-temperature treatment of antimonic acid solutions.[235] The composition of the gels prepared varies, depending on the time of drying, from $Sb_2O_5 \cdot 6 \cdot 4H_2O$ to $Sb_2O_5 \cdot 3 \cdot 4H_2O$.[235] The wet precipitates are easily dissolved in H_2O[226,227,236] or are peptized. It is difficult to dissolve products dried for a long period,[226] and also to reach equilibrium between the solid and the solution.[226] The latter phenomenon is caused by depolymerization, involving hydration, from a higher polymer to a lower one. On prolonged aging in H_2O or in Sb(V) solutions,[226,227,236,237,238] a gradual change to the crystalline form occurs, which is connected with a spontaneous condensation of OH groups.[227] The amorphous gels gradually dehydrate on heating,[233]

---

* This is the statement made by the authors of the paper cited and appears to be based on the fact that the unit cell contains 6 OH^- groups per Na^+ [Ed.].

and this change is accompanied by a decrease in the exchange capacity.[226] The following structure is proposed for the amorphous material:[225]



The exchange capacity varies, depending on the composition of the exchanger and the nature of the exchanging ion (Na^+—4·2 meq/g, Sr^{2+}—1·8 meq/g).[234]

The glassy form of antimonic acid ($Sb_2O_5{\cdot}nH_2O$) is prepared by hydrolysis of $SbCl_5$ solutions and dissolution of the fresh precipitate in hot water, followed by rapid cooling.[225,226] The glassy gel obtained gives five weak X-ray powder pattern lines and its properties are very similar to those of amorphous antimonic acid.[225,226]

Some other methods of preparation leading to products of different properties have been described.[239] (Oxidation of $SbCl_3$ with nitric acid or *aqua regia* and subsequent hydrolysis or neutralization of the acid solutions of Sb(V) salts with ammonia).[239]

Antimonic acid acts as a cation-exchanger. An equivalent exchange has been found for various univalent and bivalent metal cations.[227,228,239,240,241] Titration curves show one inflection point[239,248] with p*K* values varying from 2·34 to 3·18, depending on the method of preparation.[239] The shape of the titration curves does not depend on the strength of the base.[228] Ion-exchange equilibria of alkali metal ions, alkaline earth, metal ions Ag^+, Ce^{3+}, La^{3+}, Eu^{3+} and Th^{4+} have been studied.[230,231,238,239,243] The affinity series for alkali and alkaline earth metal cations vary depending on the crystalline form of the exchanger as well as on the sorption media. The series $Li < Na < K < Rb < Cs$ in acid solutions and $Li < Na \sim Cs < K = Rb$ in NH_4NO_3 solutions were found for both the amorphous and glassy exchangers.[238] For the crystalline material the following series were found: $Li < K < Cs < Rb < Na$ in acid solutions, $Li < K < Rb < Cs < Na$ in NH_4NO_3 solutions.[238,243] The affinity series for micro amounts of alkali metal cations confirms the decreased order of the lattice constants of various alkali metal forms of the exchanger[238] except for Li^+. However, slightly different affinity series have been reported by other authors for crystalline antimonic acid: $Cs < Li < Rb < NH_4 < K < Na$[231] and $Rb{=}Cs < Na$.[230] Similar disagreement between various authors exists for the alkaline earth metal cation series: $Mg < Ca < Sr < Ba$,[231] $Ra < Ba < Ca < Sr$.[230]

Ion-exchange isotherms measured for the systems alkali metal ion $-H^+$, Ag^+-H^+, $Ca^{2+}-H^+$, $Sr^{2+}-H^+$, $Ba^{2+}-H^+$, $Pb^{2+}-H^+$ and $La^{3+}-H^+$ are mostly S-shaped,[230,231,238,239] indicating selectivity reversal. From the dependence of selectivity coefficients on the exchanger loading, thermodynamic equilibrium constants and ΔG values have been calculated[230] for various systems and are presented in Table II. The selectivity coefficients decrease with exchanger loading. Plots of log selectivity coefficient *vs.* exchanger composition are linear up to 65% of available capacity, indicating that 9 of the 14 hydrogen ions in the unit cell are attached by the exchange. In terms of the proposed

TABLE II.—THERMODYNAMIC EXCHANGE DATA FOR CRYSTALLINE ANTIMONIC ACID.[230]

System	ln K	ΔG, *kJ/g ion*
Na^+–H^+	−7·4	+18·1
Ag^+–H^+	3·53	−8·4
Tl^+–H^+	3–4	−8
Ca^{2+}–H^+	−4·7	+ 5·7
Sr^{2+}–H^+	0	0
Ba^{2+}–H^+	−8·7	+10·6
Pb^{2+}–H^+	2·30	−3·2
La^{3+}–H^+	−64	+52

polymeric structure[230] this is explained as follows: the 9 exchange sites on the trimeric antimony species are the most reactive and may be considered as ionized sites neutralized by free hydrogen ions, while the 5 remaining sites associated with the pentameric unit consist of covalently-bound hydrogen ions which can only be exchanged by large ions at rather low acidity. Ions such as Ag^+ are covalently bound with formation of Ag–O–Sb bonds attaching the 5 remaining sites having a covalent bond nature.[230] The exchange is then partly irreversible (the residual amount of ~2 meq of Ag per g cannot be eluted).[230]

Owing to the large differences in the selectivity for individual alkali metal cations, these ions can be separated on a small column with nitric acid or ammonium nitrate solution as eluent.[243] However, the glassy and crystalline materials are more favourable for column separations, owing to their low solubility and suitable granular form.[238] Li, Na and K can be separated on amorphous and glassy materials, and a mixture of Li, K and Cs on the crystalline material by elution with nitric acid. Similarly, neighbouring pairs, except Rb–Cs, are easily separated[238] by NH_4NO_3 elution.

Miscellaneous applications[43] of antimonic acid such as column separation of ^{90}Sr from the fission products mixture,[244] ^{90}Sr recovery from acid solutions after nuclear fuel reprocessing[242,245] and separation of Na^+ in activation analysis,[246] have been reported.

Phosphoantimonic acid

A highly temperature- and radiation-resistant exchanger based on antimonic acid—phosphoantimonic acid—is formed by pouring $SbCl_5$ into phosphoric acid[241,247] or by treating Sb(V) salt solutions with phosphoric acid and then neutralizing with ammonia.[248,249] The resulting glassy solid, with variable P/Sb ratio, is not attacked by water, salt solutions or strong acids.[247,250] The selectivity of this exchanger depends on the P/Sb ratio in the solid.[251,252,253] Samples with a high P content are selective for univalent cations such as Na^+, K^+, NH_4^+ and Ag^+.[252] Reversible exchange was found for various systems, *i.e.*, alkali metal ion–H^+, NH_4^+–H^+, Ag^+–H^+, alkaline earth metal cations –H^+, Cu^{2+}–H^+, Ce^{3+}–H^+, K^+–NH_4^+, $Ag(NH_3)_2^+$–NH_4^+.[242,247,250] The titration curve of phosphoantimonic acid shows one sharp inflection point, indicating the exchanger to be a strong monobasic acid.[250,253] This exchanger (as well as the exchanger with H_2TeO_4 incorporated instead of H_3PO_4) has been reported[248,249] as a suitable material for the separation of alkaline earth metals and lanthanides from alkali and transition metals.

Other hydrous oxides of this group

Little attention has been given to other hydrous oxides of quinque- and sexi-valent metals. Hydrous V_2O_5[254] in mixture with hydrous zirconia adsorbs K^+, Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+} and Ag^+. Its total exchange capacity is between 1·42 and 1·95 meq/g, depending on the V content of the mixture, and is reduced by thermal treatment. Hydrous Nb_2O_5 acts both as cation-[241] and anion-exchanger[255,256,257] selective for $Cr_2O_7^{2-}$, paramolybdates, tungstates and ferrocyanides. Hydrous Ta_2O_5 is a cation-exchanger[241,258,259] suitable for the purification of nuclear reactor cooling-waters at high temperatures up to 300°.[258,259] The hydrous oxides of Mo(VI) and W(VI) act as cation-[241] or as anion-exchangers in mixtures with basic hydrous oxides.[260]

ACIDIC SALTS OF MULTIVALENT METALS

A wide range of compounds of this type has been described as ion-exchangers. Among the metals studied have been zirconium, thorium, titanium, cerium(IV), tin(IV), aluminium, iron(III), chromium(III), uranium(VI) *etc*, and the anions employed include phosphate, arsenate, antimonate, vanadate, molybdate, tungstate, tellurate, silicate, oxalate *etc*. These salts, acting mostly as cation-exchangers, are gel-like or microcrystalline materials, with the composition and properties depending upon the method of preparation, and possess mostly a high chemical, temperature and radiation stability.[1,2,3] The cation-exchange properties arise from the presence of readily exchangeable hydrogen ions, associated with the anionic groups present in the salts. Some of these materials also exhibit electron-exchange properties.

Recent developments in study of these materials have led to a successful preparation of defined crystalline compounds of the type $M^{IV}(HX^{V}O_4)_2 \cdot yH_2O$ and to recognition of their crystal structure. The structure is layered and the crystalline compounds exhibit ion-sieve properties.[286] Knowledge of the crystal structure gave a deeper understanding of the ion-exchange processes and their reversibility[314] as well as a solid basis for the interpretation of thermodynamic measurements.[293,322] Besides possible application of these exchangers in chemical processing of radioactive materials and in treatment of contaminated moderator- and cooling-water in nuclear reactors working at high temperatures and pressures, new applications have recently been found, such as in water desalination processes and in fuel-cells employing ion-exchange membranes for transport of hydrogen ions.

Acidic salts of quadrivalent metals

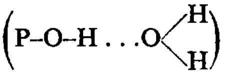
These substances have been the most intensively studied group of synthetic inorganic ion exchangers. Most of the work to date has been concerned with zirconium phosphate exchangers, which have been more thoroughly studied than any of the other materials.

Zirconium salts

Zirconium phosphate. The earlier studies on zirconium phosphates (ZrP) were mostly concerned with the amosphous materials.[1,2,3,261] The interest during the last five years has been primarily in the semicrystalline and crystalline forms of zirconium phosphates. Owing to their definite structure, a more exact interpretation of the sorption phenomena might be achieved. However, the applications of amorphous materials are still of great interest.

The preparation of gelatinous amorphous sorbents was carried out by the usual mixing of Zr salt solutions with phosphoric acid at room temperature. According to the preparation conditions, materials with P/Zr ratios of 0·5–2·1 were formed.[1,262–267,373] A granular material was prepared by freezing the gels at up to $-22°$.[268,269] Thermal treatment of amorphous materials with phosphoric acid[270,271,272] or refluxing them with $\geqslant 2{\cdot}5M$ phosphoric acid[1,271,273–275] leads to the formation of semicrystalline or crystalline forms, respectively. In the latter case, the well developed crystalline phase of the so-called α-ZrP was prepared, corresponding to the formula $Zr(HPO_4)_2{\cdot}H_2O$. The same compound resulted after evaporation of suitable Zr salt solutions with hydrofluoric acid.[276] A β-phase and a γ-phase, corresponding to $Zr(HPO_4)_2$ and $Zr(HPO_4)_2{\cdot}2H_2O$ respectively, were prepared by refluxing the solutions of $ZrOCl_2$ with NaH_2PO_4 in $3M$ hydrochloric acid. Drying over anhydrous $CaSO_4$ leads to the formation of β-ZrP; air-dried products correspond to γ-ZrP.[277] The surface area of the crystalline preparations is about 1000 times that of the amorphous ones.[278,279]

The composition of amorphous or poorly crystalline materials is mostly interpreted in terms of compounds for which the P/Zr ratio is freely variable, without existence of distinct, more definite intermediate products,[280] and the P/Zr ratio found is then speculatively ascribed to corresponding hypothetical formulae such as $Zr(OH)(PO_4)$, $ZrO(HPO_4)$, $Zr_3(PO_4)_4$, $Zr(HPO_4)_2{\cdot}xH_2O$ and $Zr(HPO_4)(H_2PO_4)(OH)$.[270,271,281]

An attempt has been made to solve the structure of α-ZrP.[282–285] A three-dimensional study on $Zr(HPO_4)_2{\cdot}H_2O$ single crystals, presented by Clearfield and Smith[286,287,288] resolved this structure completely from the integrated precession data; α-ZrP crystals are monoclinic with $a = 0{\cdot}9076$, $b = 0{\cdot}5298$, $c = 1{\cdot}622$ nm and $\beta = 111{\cdot}5°$. There are 4 formula units per unit cell and the space group is $P2_1/c$. The structure is layered and consists of a sheet of roughly coplanar Zr atoms sandwiched between two sheets of monohydrogen phosphate groups. Each Zr atom is co-ordinated octahedrally to 6 oxygen atoms. Each of these 6 oxygen atoms belongs to one of six different monohydrogen phosphate groups. This group acts as a 3-way bridging ligand, co-ordinating 3 different Zr atoms through 3 of its oxygen atoms. The fourth non-co-ordinating oxygen atom points towards an adjacent layer in the structure and presumably bears the H atom. The forces between layers are very weak long hydrogen-bonds or van der Waals forces and the interlayer distance is 0·76 nm. The layers are arranged relative to each other in such a way that the Zr atoms in one layer lie over the P atoms in an adjacent layer and *vice versa*. Zeolitic type cavities are thus formed. There is exactly one such cavity per formula unit of α-ZrP. A water molecule resides in the centre of each cavity and is hydrogen-bonded to phosphate groups. A schematic illustration of two adjacent layers in α-ZrP with the formed cavity is presented on Fig. 2.[286] One possible speculative arrangement of the hydrogen-bonds is that in which one H atom of a phosphate group is directed towards the H_2O molecule  $\left(P{-}O{-}H\ldots O\!\begin{smallmatrix}\diagup H\\ \diagdown H\end{smallmatrix}\right)$ forming the interlayer bonds. The remaining hydrogen-bonds form very weak interlayer bonds (P–O–H . . . O–P) and form a zigzag array running parallel to the *b*-axis.[286] This

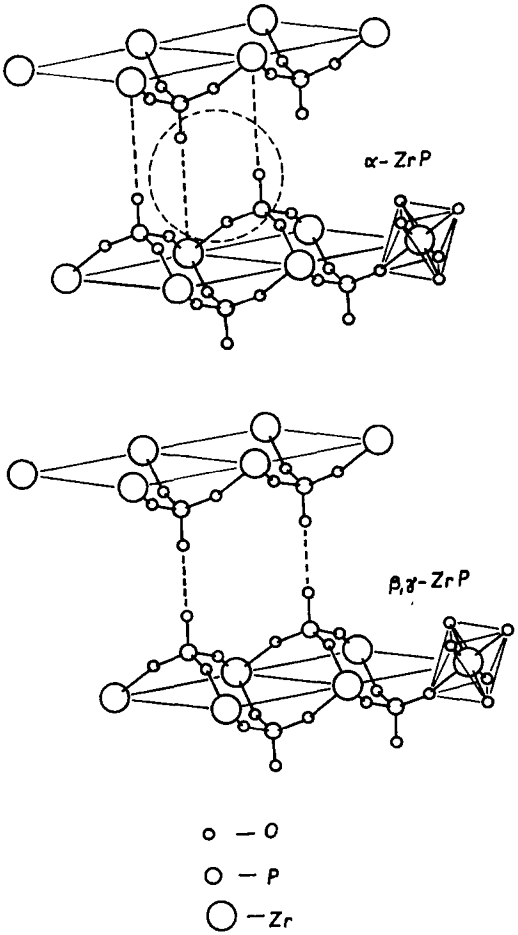
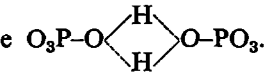


FIG. 2.—Schematic illustration of the structures of α-, β-, and γ-ZrP.[277]
Dashed circle—inter-layer cavity.

idea is in agreement with the infrared measurements on α-ZrP and its deutero-analogues.[289] Structural features of the β-phase are essentially the same as those of α-ZrP but with a different interlayer distance, 0·928 nm. It has been proposed that the layer packing sequence is such that neighbouring HPO_4 groups from adjacent layers are aligned opposite one another (Fig. 2) to allow interlayer hydrogen-bonds of the type  $O_3P{-}O\langle\overset{H}{\underset{H}{}}\rangle O{-}PO_3$. The structure of γ-ZrP is very closely related to that of β-ZrP. The interlayer attractions are probably hydrogen-bonds between the aligned HPO_4 groups through the interagency of the water molecules. The interlayer separation must be thus substantially larger than that in β-ZrP.[277]

The hydrolytic behaviour of these ion-exchangers is closely connected with their structure. The tendency towards hydrolysis decreases from amorphous to crystalline ZrP.[283,290] The stability of the H^+ forms of amorphous ZrP with respect to phosphate release increases with decreasing P/Zr ratio.[291,373] The stability increases in the presence of ions, in the following order: Li $<$ Na $<$ Ag $<$ K $<$ Rb $<$ NH_4 $<$ Cs. With the Li and Na forms of the ZrP cation release prevails, while with the K, Rb, and Cs forms, phosphate release predominates.[264,292] At low pH, the phosphate release is not primarily due to a "hydrolysis," but rather to washing out of phosphoric acid, which adheres very stubbornly to the gel,[272] or to a conversion into a less acidic compound on aging the gel: $2Zr(HPO_4)_2 \rightleftharpoons Zr_2H(PO_4)_3 + H_3PO_4$.[293] In this way a linear dependence of the equilibrium phosphate concentration in the solution on the weight of amorphous solid material, may be explained.[289,290] The solubility data of crystalline ZrP in strong phosphoric acid have been determined.[294]

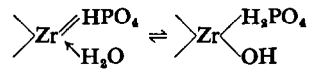
The changes occurring on heating the ZrP sorbents have been studied quite intensively.[267,295,374] Anhydrous $Zr(HPO_4)_2$ was obtained by heating at up to 130°.[278,296] The loss of constitutional water and formation of pyrophosphate groups start at $\sim$180°.[296,297] At 200° about 13·8% of the total capacity is lost,[296] but the degree of cross-linking increases and variations in selectivity occur.[267,289,297,298,299] No condensation was observed on similar thermal treatment of crystalline and semicrystalline materials, even on autoclaving under pressure at 270°. However, $Zr_3(PO_4)_4$ formation was found in the case of amorphous materials.[290,300,301] By 450° the capacity of crystalline samples has decreased to 58·8% of the starting value[296] and at 550° ZrP_2O_7 is formed.[278] Crystalline ZrP in the K^+ form is converted into $Zr(KPO_4)_2$ after heating to 1000°. Ammonium forms are decomposed at elevated temperatures and the pure H^+-form of the sorbent is created.[266,302]

Sorption properties of both amorphous and crystalline ZrP have been extensively studied by many authors. Great attention has been paid to the alkali metal cations.

The adsorption on the amorphous ZrP gels, especially those of high P/Zr ratio ($>$1·5), is an ideal cation-exchange.[292] The capacity increases with the P/Zr ratio.[262] It is supposed from the titration curves that monobasic[303] as well as dibasic[262,271,304] acid groups are present in these gels. The points of zero charge vary significantly with the composition of the gels.[305] At lower P/Zr ratios, however, these gels retain part of the amphoteric character which is connected with the presence of the hydrous ZrO_2 functional groups.[292,318] It has been proved that K^+ and Li^+ are attracted electrostatically to the surface of the solid only when the solid is negatively charged; on the other hand, ions which form insoluble phosphates, such as Ag^+, are chemisorbed even when the solid is positively charged.[306] The adsorption phenomena are closely connected with the water content of the sorbents. It has been confirmed by Ahrland[298] that the affinity of amorphous ZrP for Cs adsorption considerably increases when the gels are dehydrated to one mole of water per mole of Zr in the sorbent. A similar but less marked increase occurs for Na.[272,374] The selectivity for K, Rb and Cs adsorption is rather higher than that for Li, Na and Ag and increases with increasing P content in the sorbent.[292,307] The Cs adsorption is very little influenced by temperature increase[198] and diffusion phenomena are the decisive factors for the rate of exchange.[309] Cs adsorption substantially increases in the presence of the phosphate ions in the solution. The ion-exchange process is thus more complicated than simple ion-exchange and structural changes in the sorbent during the adsorption process have to be taken into account.[290]

Very interesting phenomena have been found on studying the adsorption on α-ZrP. The titration curves for the exchange of Li^+, Na^+ and K^+ for H^+ exhibit a hysteresis loop. A marked hysteresis has also been found in the Na–Li and Li–K exchange processes.[310] The hysteresis results from the presence of different phases in the forward and reverse titrations. When α-ZrP is titrated with NaOH, two solid phases are present up to 50% exchange, *i.e.*, α-ZrP and the compound $Zr(NaPO_4)(HPO_4)\cdot 5H_2O$. At higher levels of exchange another two-phase region is obtained, *i.e.*, the latter compound and a fully exchanged phase with composition $Zr(NaPO_4)_2\cdot 3H_2O$. The interconversion of these phases is fully reversible. However, when the half-exchanged phase takes up protons it forms an unexchanged phase, which is more highly hydrated than the original α-ZrP.[311] In the case of Li^+ exchange, phases of composition $Zr(LiPO_4)_{1\cdot 33}(HPO_4)_{0\cdot 67}\cdot 4H_2O$ and $Zr(LiPO_4)_2\cdot 4H_2O$ are formed.[312] The process of H^+–Li^+ exchange is accompanied by a substantial particle size decrease with increasing loading of the exchanger.[276] Kinetic measurements by Nancollas *et al.*[313] led to the conclusion that the Na^+–H^+ exchange process rate is governed by the diffusion rate of ions through the exchanger particles. The diffusion coefficients of alkali metal cations decreased in the order K > Na > Li.[305]

The detailed ion-exchange mechanism for crystalline ZrP has now been presented by Clearfield. Even though the existence of two tautomeric forms[278]



or formation of different functional groups as a function of pH[271] can be used to explain some sorption phenomena, the model based on the layer structure properties of crystalline ZrP was found to be the most exact. The zeolitic nature of the crystals and the weak forces between layers provide a basis for explaining their sieving behaviour and the ready expansion of the lattice during exchange.[286] Both phosphate hydrogen ions are replaceable by cations, so the capacity of the exchanger is 6·64 meq/g. One proton is exchanged at the relatively low pH of 2–4 by alkali metal cations, and the interlayer distances remained unchanged (0·76 nm). Thus at half the exchange capacity, all the cavities contain one univalent cation and can accommodate no more. The second proton exchanges at higher pH and the cations insert themselves between the layers, with consequent spreading apart of the layers. Thus the mechanism of exchange is thought to involve the diffusion of unhydrated (or partially hydrated) ions into the cavities (0·24 nm in diameter), replacing the more acidic phosphate protons. This is followed by diffusion of water molecules into the crystal lattice and subsequent rehydration of the cations. Further exchange can then occur by diffusion of hydrated ions into the sorbent cavities.[314] Li^+ and Na^+ are exchanged as the hydrated ions and K^+ as the unhydrated ion.[305] The interlayer separation of 0·76 nm disappears when Sr^{2+} is sorbed and the unhydrated ions immediately occupy sites between the layers rather than inside the cavities. The exchange of Ba^{2+}, however, involves breaking of hydrogen bonds, hydration of the resultant protons, dehydration of the incoming cations, and co-ordination of the cations within the crystal lattice with consequent enlargement of the interlayer separation.[287] The interlayer distances in the half-exchanged forms decrease in the order Li > Na > K[305] and have the following values (in nm) for substitution of the species named: Sr–1·02,[287] n-hexylammonium–2·28,[315] n-octadecylammonium–4·70,[315] $Zr(LiPO_4)_{1\cdot 33}(HPO_4)_{0\cdot 67}\cdot 4H_2O$–1·00,[312] $Zr(LiPO_4)_2\cdot 4H_2O$–1·01,[312] $Zr(NaPO_4)(HPO_4)\cdot 5H_2O$–1·18,[314] and $Zr(NaPO_4)_2\cdot 4H_2O$–0·98.[314] The interlayer separation in the γ-ZrP is large enough to permit the exchange of larger cations such as Cs and Ba ions, which are rather excluded by α-ZrP.[277] It is interesting to note that the α-ZrP has the ability to exchange ions directly with solids or gases.[316] The exchanger, in the hydrogen form, is heated (~150°) with an anhydrous metal salt (LiCl, NaCl, $ZnCl_2$, $MnCl_2$, $CoCl_2$, $AlCl_3$, $HfCl_4$) which on exchange forms a volatile acid (HCl). The exchange reaction proceeds by continuous removal of the volatile acid. Exchanged cations may be eluted with dilute acid solutions or removed by gaseous HCl.[316]

The selectivity of zirconium phosphates towards the bivalent cations is rather low.[292,304] Higher adsorption was found for Sr^{2+} at elevated temperature.[198] The cations such as Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are sorbed to about the same extent, and their affinity is not very different from that of Sr^{2+}.[272] UO_2^{2+} is easily adsorbed at high temperatures on amorphous ZrP.[317] The adsorption of Sr on crystalline ZrP was found to be independent of ionic strength and the interdiffusion coefficients were found to be constant.[305]

Cr^{3+} is adsorbed on amorphous ZrP a little more strongly than the bivalent ions, while the affinity towards Fe^{3+} was found to be extremely high. The uptake of this ion is not a simple exchange reaction but rather a process involving the introduction of Fe^{3+} ions into the matrix of the sorbent.[272] Small differences in selectivity of sorption on amorphous ZrP were found for Am^{3+}, Cm^{3+}, Cf^{3+}, Ce^{3+} and Eu^{3+} at 75°.[291,292] Very low adsorption of Ru occurred over the entire concentration range (0–9M) of perchloric nitric and hydrochloric acids.[304] Some of the multivalent cations, such as U^{4+}, Th^{4+}, Pu^{4+}, *etc*, are adsorbed irreversibly, probably because of precipitation of the corresponding phosphates during the adsorption process.[290,292,300,304,319] In the case of UO_2^{2+} adsorption on semicrystalline and crystalline ZrP the formation of a $UO_2HPO_4{\cdot}4H_2O$ phase has been proved by X-ray analysis.[290,300] Similarly, a relatively strong uptake of WO_4^{2-} and $Mo_7O_{24}^{6-}$ anions on amorphous ZrP may be explained by the chemical interaction between these anions and the phosphate group.[320] The thermodynamics of ion-exchange on different types of zirconium phosphates have been studied for various systems.[293,301,303,321,322] The ΔG, ΔH and ΔS values determined are summarized in Table III. Generally, the free energy changes become more positive going from amorphous to crystalline materials (for the same exchange system) indicating the latter to be less favourable for the exchange. The free-energy changes for the alkali metal ion $-H^+$ exchange[322] as a function of the radius of the ingoing cation show a departure from a linear relationship. This behaviour is interpreted in terms of increasing distortion of the ion-exchanger matrix with size of the ingoing ion. The enthalpy changes are negative for alkali and alkaline earth metal cations,[1,301,321,322] and positive for UO_2^{2+},[293] Ce^{3+} and Eu^{3+}.[1]

Even though ZrP has been the most extensively examined of all inorganic ion-exchangers of this type, there still appear new fields for its application.

First of all, the knowledge of the selectivities[323,324,325] and affinity sequences is useful for rough evaluation of the separation possibilities. The affinity sequences can be summarized as follows: amorphous ZrP: $Cs > Rb \gg K > Na$,[267] $Cs > Rb > Eu^{3+} > Sr^{2+}$,[303] $Co < Ni < Cu > Zn$,[272] $Ce > Y > Cr$,[272] and $Cf > Eu > Cm > Am > Ce$;[291] semicrystalline ZrP: $Li < K < H < Cs$;[322] crystalline ZrP: $Sr \geqslant UO_2 \geqslant Ce^{3+} > Na > Cs$.[284]

The following separation applications have been presented: purification of reactor coolants;[326] decontamination of D_2O;[198] decontamination of radioactive

TABLE III.—THERMODYNAMIC DATA FOR EXCHANGE ON H-FORM ZIRCONIUM PHOSPHATE

System	Temperature, °C	Amorphous ZrP			Semicrystalline ZrP			Crystalline ZrP			Reference
		$\Delta G°$, *kJ/mole*	$\Delta H°$, *kJ/mole*	$\Delta S°$, *J/mole/K*	$\Delta G°$, *kJ/mole*	$\Delta H°$, *kJ/mole*	$\Delta S°$, *J/mole/K*	$\Delta G°$, *kJ/mole*	$\Delta H°$, *kJ/mole*	$\Delta S°$, *J/mole/K*	
Li^+–H^+	20	8·4	0	−25							303
	25				7·8	−4·7	−42				322
Na^+–H^+	20	4·6	−11·3	−54							303
K^+–H^+	20	2·3	−23·8	−88				6·7	−22·7	−97	301,303
	25	3·0	−25·4	−125	4·2	−34·5	−129				301
					3·7	−19·4	−74				322
	50	6·5	−25·4	−126	7·9	−34·5	−131				301
	80	10·8	−25·4	−128	11·5	−34·5	−130	12·2	−22·7	−99	301
Rb^+–H^+	20	−9·9	−40·7	−106							303
	25	−1·4	−31·8	−103							1
	40	0	−31·8	−103							1
Cs^+–H^+	20	−12·0	−45·8	−118	−10·9	−43·0	−105				303,321
	25	−3·9	−36·8	−110	−1·6	−18·7	−67				1,322
	40	−2·2	−36·8	−110							1
	100				−0·04	−43·0	−105				321
	200				11·2	−43·0	−113				321
NH_4^+–H^+	20	−8·0		−100							303
Ca^{2+}–H^+	20	8·1	−3·6	−3·9							1
Sr^{2+}–H^+	20	7·1	−7·2	−46							1
UO_2^{2+}–H^+	25	12·5	37·3	83	18·9	40·5	73				293
	50	10·7	37·3	82	16·2	40·5	79	26·2	52·0	80	293
	80	10·6	37·3	76	10·8	40·5	84	15·3	52·0	109	293
	250	−6·4	37·3	84	0·7	40·5	79	14·0	52·0	73	293
Ce^{3+}–H^+	20	6·6	4·4	−4·0							1
Eu^{3+}–H^+	20	4·8	2·7	−7·0							1

waste water;[327] ^{137}Cs from reprocessing solutions;[328–331] Cs–Sr–UO_2;[332] Cs–Sr, UO_2, Ce, Y, $RuNO^{3+}$, Ru^{4+};[319] Cs–Ba;[329] Na–K–Rb–Cs;[267] ^{45}Ca–^{46}Sc;[333,334] Ca–Sr–Ba;[335] Ca–Sr;[334] Sr from radioactive waste water;[303] Sr–Cs[269] Sr–Ba;[269] Sr–Ce, Eu, Zr^{4+}, Pu^{4+};[319] Sr–Y–Cs;[317] Sr–Y;[269] ^{137m}Ba–^{137}Cs;[336] Ni–Co;[337] Ni–Co–UO_2–Fe^{3+};[337] Cd–Zn–UO_2–Fe^{3+};[337] UO_2–Sr;[319] UO_2, Ce, Eu–Zr^{4+}, Pu^{4+};[319] Fe^{3+}, Mn, Ni, Pb, Al, Cr^{3+}, Co–Zn, Ag, Cd;[338] Pu^{4+} from irradiated U;[319] Pu–Cs, Sr, Eu, Ce, Ru^{4+};[319] Pu, U, Cm–Yb, Fe^{3+};[339] Bk^{4+}–Cm^{3+};[291] U^{6+}–Am^{3+};[291] $CH_3(CH_2)_7NH_3{}^+Cl^-$–$CH_3CH_2NH_3{}^+Cl^-$–$CH_3NH_3{}^+Cl^-$–$Cl^-NH_3{}^+CH_2CH_2NH_3{}^+Cl^-$;[340] $(OHCH_2CH_2)_3NH_3{}^+Cl^-$–$OHCH_2CH_2NH_3{}^+Cl^-$–$NH_4{}^+Cl^-$;[340] XeO_3–HIO_3.[341]

Various applications have been made of ZrP materials used in ion-exchange membranes especially in H/O fuel cells and electrodialysis.[342–350]

Attempts have also been made to prepare inorganic ion-exchangers consisting of a combination of the zirconium phosphate compounds with another organic or inorganic component. The selectivity of such materials is supposed to be increased. The following combinations have been described: zirconium phthalophosphate,[338] zirconium sulphosalicylophosphate,[351] zirconium phosphate-silicate,[339] zirconium-niobium phosphate,[352] zirconium phosphate–ammonium molybdophosphate,[330,466] and zirconium phosphate-tungstophosphate.[328,329]

Zirconium pyrophosphate, polyphosphates and hypophosphate. Zirconium pyrophosphate is prepared by mixing zirconyl salt solutions with $Na_4P_2O_7$ in nitric acid media.[308,353] Glass-like gels of different compositions ($P/Zr = 2{\cdot}0, 2{\cdot}5–2{\cdot}8$) are formed. By freezing of the precipitated gel, products of better mechanical properties may be obtained.[354] The exchange capacities vary according to the drying temperature, time of aging[465] and the exchanger composition.[353] The selectivity for various cations follows the order $Cu > Ni > Ca > Na \gg Fe^{3+} > Mg$[353] and an ion-exchange mechanism has been shown to operate for adsorption of Cs^+ and Sr^{2+}.[308] The following separations have been successfully achieved with this exchanger: ^{90}Sr–^{90}Y; ^{90}Sr from ^{90}Y, ^{137}Cs; $UO_2{}^{2+}$–^{234}Th; Pu^{4+} from $UO_2{}^{2+}$, ^{95}Zr, ^{95}Nb, ^{106}Ru, ^{144}Ce, ^{90}Sr, ^{137}Cs;[308] Cd^{2+}–Cu^{2+}; Pb^{2+}–Hg^{2+}; Mg^{2+}–Cd^{2+}; Ag^+–Hg^{2+}; Ni^{2+}–Fe^{3+}; Fe^{3+}–Zn^{2+}; Fe^{3+}–Cu^{2+}.[355]

Various *zirconium polyphosphate* products are obtained by mixing zirconyl salt solutions with sodium polyphosphates of various degree of polymerization.[356,357] The exchange capacity increases with increasing degree of polymerization of the starting phosphate material.[356] However, a higher amount of polyphosphate in the solid affects the kinetics of the adsorption, owing to a higher degree of cross-linking.[357] The $NH_4{}^+$ form of the exchanger is selective for alkali metal cations,[358] and has been used for their separation and purification.[359] The H^+ form is selective for Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Ni^{2+}, Sn^{2+} and Sb^{3+} ions.[360]

By mixing $ZrOCl_2$ and $Na_2H_2P_2O_6$ solutions in hydrochloric acid, amorphous *zirconium hypophosphate* ($Zr:P = 1:1{\cdot}75$) is formed, which is highly selective for multivalent cations.[361,362,363] Support-free thin sheets made from zirconium hypophosphate have been used for the chromatographic separation of Sn^{2+}, Pb^{2+} and tervalent cations from alkali, alkaline earth and bivalent transition metal cations.[361]

Zirconium arsenate and antimonate. Zirconium arsenate is prepared either as an amorphous substance by mixing zirconium salt solutions with arsenic acid[364,365,366] or as a crystalline material by refluxing the amorphous zirconium arsenate with H_3AsO_4 for a prolonged period.[364,365]

The amorphous materials, of various As/Zr ratios (1·53–1·96), in comparison with the crystalline materials exhibit very low stability towards hydrolysis at higher pH[364] and their titration curves do not exhibit any particular inflection point, suggesting that the exchangeable hydrogen ions display a range of acidities.[364] The affinity series for alkali metal cations changes with pH (Cs > K > Na at pH 2·6, Na > K > Cs at pH 4·65).[365]

The crystalline zirconium arsenate, $Zr(HAsO_4)_2 \cdot H_2O$,[364,365] is isomorphous with α-zirconium phosphate. The parameters of its monoclinic lattice are $a = 0·9178$ nm, $b = 0·5378$ nm, $c = 1·655$ nm, $\beta = 111·30°$, and the average As–O and Zr–O distances are close to those in α-zirconium phosphate.[367] One molecule of water is reversibly lost on heating at 110°, without changing the X-ray patterns;[364,365] on heating to 500°, the second water molecule is lost owing to the condensation of $HAsO_4^{2-}$ groups. On titration with LiOH, NaOH and KOH, two end-points occur in the titration curves, corresponding to the replacement of the two hydrogen ions of the two $HAsO_4^{2-}$ groups.[364,365] Practically no adsorption of Cs^+ occurs in acid solutions up to pH 7; at higher pH, however, some exchange is observed, accompanied by remarkable hydrolysis of the exchanger and destruction of its crystal structure.

The ion-exchange process is assumed to proceed as follows: during the replacement of the first hydrogen ion the exchanging ions occupy the zeolitic cavities in the crystal (one cavity per Zr atom) and the interlayer distance remains unchanged.[364] Only Li^+, Na^+ and K^+ are small enough to enter these cavities.[365] When one mole of hydrogen ions per formula weight of the exchanger has been replaced, the ingoing cations must insert themselves between the layers, which is demonstrated by the increase in interlayer distances of the totally exchanged Li^+, Na^+ and K^+ forms as compared with the H^+ form. These distances indicate that the unhydrated cations are exchanged, since the increased interlayer distances are only slightly larger than the diameters of the inserted cations.[364] Such a behaviour indicates that crystalline zirconium arsenate exhibits ion-sieve properties, similarly to the other crystalline salts of this type.

The Na^+–H^+, Tl^+–H^+ and Ba^{2+}–H^+ exchange processes have been found to be irreversible,[365] owing to the structural rearrangement when going from the H^+ to M^+ form or to a possible precipitation of barium arsenate within the exchanger.

Amorphous zirconium arsenate has been reported as a suitable material for concentrating caesium from a mixture containing multivalent and alkali metal ions.[368]

Zirconium antimonate is prepared as an amorphous substance by mixing $ZrOCl_2$ solutions with an excess of Sb_2O_5 dissolved in hydrochloric acid.[369] From the exchange isotherm measurements the affinity series Na ⩾ K > NH_4 > Rb > Cs > Li has been established.[370] The exchange reaction rate increases from Li^+ to Cs^+.[370] Mutual separation of Rb^+ and Cs^+ [371] and separation of microquantities of Na^+ from macroamounts of Al^{3+} have been described.[369]

Zirconium molybdate and tungstate. Zirconium molybdate is prepared by mixing zirconyl salt solutions with ammonium molybdate and subsequent neutralization with ammonia. Amorphous products of various composition with the Zr/Mo ratio ranging from 0·5 to 2·0 are obtained, depending upon the pH of the precipitation.[263,372] Their ion-exchange capacities for K^+ and Cs^+ lie between 2·18 and 2·43 meq/g.[372] Zirconium molybdate also exhibits electron-exchange properties, *e.g.*, its ability to oxidize $SnCl_2$ solutions. The mean value of the electron-exchange capacity is 0·18 meq/g.[372]

Zirconium tungstate is prepared by mixing zirconium salt solutions with Na_2WO_4[373,375] or by passing a concentrated Na_2WO_4 solution through an anion-exchange column filled with hydrous ZrO_2. Amorphous products of various composition (Zr:W = 1·0–0·44)[263,375] and properties were obtained. They are easily soluble in strong acids.[373,374] The selectivity for alkali metal cations decreases in the order Cs > Rb > K > Na > Li.[376] An equivalent UO_2^{2+}–H^+ exchange has been reported for gels pretreated with 1*M* nitric acid.[374] Similarly to zirconium molybdate, zirconium tungstate can act as an electron-exchanger.[375] It is reduced by $SnCl_2$ solutions, probably to products containing tervalent W. The reduced form can be reoxidized by Fe^{3+}, Ce^{4+}, V(V) or H_2O_2 solutions. The electron-exchange capacity is 0·26 meq/g.[375]

Zirconium tellurate, oxalate and silicate. Zirconium tellurate is prepared by refluxing $ZrOCl_2$ and Na_2TeO_4 solution in 1*M* hydrochloric acid[377] and its composition corresponds to the formula $Zr(H_2TeO_6)·4H_2O$.[377] Four molecules of water are lost on heating to 100–500°; at 650–700° condensation to $Zr(TeO_5)·H_2O$ occurs.[377] The exchange capacity determined from the titration curves (~2·8 meq/g)[377,378] is approximately one half of the formula capacity, indicating that only 50% of the H^+ ions are exchangeable in the pH range of 2·5–12.[277]

Gel-like and crystalline *zirconium oxalates* of empirical formula $ZrO(OH)C_2O_4H$ were prepared from $ZrOCl_2$ and $(NH_4)_2C_2O_4$ solutions.[379] An unusual affinity series has been reported for alkali metal cations: Na < Cs < Rb < K.[379]

Zirconium silicate with total exchange capacity 3·18 meq/g[380] has been used for the separation of Th^{4+} from Sm^{3+} and of Ca^{2+} from Sr^{2+}.[381]

Thorium salts

Of the thorium salts only phosphate, arsenate and molybdate have been reported as ion-exchangers.

Thorium phosphate with variable composition, low stability towards hydrolysis and low exchange capacity is prepared by precipitation at room temperature. However, by precipitation at 100° and subsequent digestion for 40 hr, fibrous crystalline materials (similar to fibrous cerium phosphate) are obtained.[382] The exchange capacity for Na^+ (3·7 meq/g) is closed to that corresponding to the stoichiometric formula $Th(HPO_4)_2·3H_2O$. This material is suitable for preparing support-free ion-exchange sheets having potential application in electrophoresis.[382]

Thorium arsenate is prepared by prolonged refluxing of thorium nitrate solution in arsenic acid at 110°.[383] Crystalline material of composition $Th(HAsO_4)_2·H_2O$[384] is not readily dissolved at pH < 12.[383] The exchanger is highly selective towards Li^+ ions; Na^+, K^+, Rb^+, Cs^+ and Tl^+ are not adsorbed at all. This behaviour is due to an ion-sieve effect of this compound, which has the smallest interlayer distance of all the compounds of this type. A comparison of ion-sieve behaviour of various compounds of the type of $M^{IV}(HXO_4)_2·yH_2O$ is given in Table IV. The Li^+ form of thorium arsenate possesses a similar crystal structure to that of the H^+ form, and the exchange process, unlike that of other salts of this type is completely reversible.[384] Two phases, $Th(HAsO_4)_2·H_2O$ and $Th(LiAsO_4)_2·H_2O$, are present at each stage of the exchange process.

Thorium molybdate is prepared by mixing $Th(NO_3)_4$ and Na_2MoO_4 solutions.

TABLE IV.—COMPARISON BETWEEN THE FIRST INTERPLANAR DISTANCE AND ION-EXCHANGE PROPERTIES OF THE SALTS OF THE TYPE $M^{IV}(HXO_4)_2yH_2O$

Exchanger	First interplanar distance, *nm*	Alkali metal cation exchanged by the H^+ form
$Zr(HPO_4)_2 \cdot 2H_2O$(γ–ZrP)	1·220	Na—Cs
$Th(HPO_4)_2 \cdot 3H_2O$	1·147	Na—Cs
$Ce(HPO_4)_2 \cdot H_2O$	1·095	Li, Na, K, Rb, Cs
$Zr(HPO_4)_2$ (β–ZrP)	0·940	Na—Cs
$Ce(HAsO_4)_2 \cdot H_2O$	0·910	Li, Na, K (partly)
$Zr(HAsO_4)_2 \cdot H_2O$	0·780	Li, Na, K, Cs (partly)
$Sn(HAsO_4)_2 \cdot H_2O$	0·777	Li, Na, K (partly) Cs (partly)
$Ti(HAsO_4)_2 \cdot 2H_2O$	0·777	Li, Na, K
$Sn(HPO_4)_2 \cdot H_2O$	0·776	Li, Na, K, Cs (partly)
$Zr(HPO_4)_2 \cdot H_2O$ (α–ZrP)	0·760	Li, Na, K
$Ti(HPO_4)_2 \cdot H_2O$	0·756	Li, Na,
$Th(HAsO_4)_2 \cdot H_2O$	0·705	Li

Various conditions of preparation lead to formation of different products.[385] This exchanger is readily dissolved in mineral acids and on heating to 100° its capacity (~0·57 meq/g) is lost. Total adsorption of Fe^{3+}, Zr^{4+} and Pb^{2+} has been observed and Co^{2+}–Fe^{3+}, Zn^{2+}–Fe^{3+} and Cu^{2+}–Fe^{3+} separations have been achieved with this exchanger.[385]

Titanium salts

Titanium phosphate. Various methods have been described for the preparation of titanium phosphate ion-exchangers, leading to formation of amorphous,[265,386,387] granular amorphous[388,389] and crystalline[276,366,390,391] products. The composition of the amorphous materials varies between P/Ti ratios of 0·6 and 2·0, and different empirical formulae such as $[(TiO)_{0\cdot535}(H_2PO_4)_{0\cdot369}(OH)_{1\cdot77}]\cdot 1\cdot 11\ H_2O$,[386] $TiH_2(PO_4)_2 \cdot 4H_2O$ and $Ti_3(PO_4)_4$[387] have been proposed for these materials. High exchange capacity has been found (~7·5 meq/g)[386] and is not appreciably affected by calcination.[392,393] The exchanger can be easily regenerated[386] and exhibits a high selectivity towards Cs^+.[386] Selectivity series for alkali metal cations reported by various authors[263,265,394] differ substantially, probably owing to different products being used.

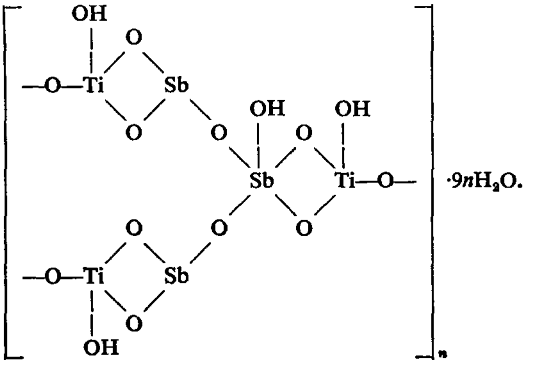
A formula $Ti(HPO_4)_2 \cdot H_2O$[366,390,391] for crystalline titanium phosphate has been proposed on the basis of chemical and X-ray analysis. One molecule of water was lost reversibly on heating this material to 120°.[366,390,391] A further molecule of water was taken up on standing in a water-saturated atmosphere at 0–20°,[366] and the product showed higher resistance than the amorphous materials towards hydrolysis.[390] The total ion-exchange capacity is 7·15 meq/g.[390] However, crystallization of the exchanger permits the exclusion of ions with larger ionic radii. This effect is more noticeable for this compound than for the zirconium phosphate, since K^+ ions are also excluded in acid solutions. By conversion into the Na^+ form, the crystallographic *d*-values are increased and the material exhibits a lower degree of crystallinity. A special behaviour has been observed for the Li^+ form, when no changes in X-ray pattern occurred on the conversion of the H^+ form into the Li^+ form, and difficulties arose in converting the Li^+ form into the K^+ and even into the Na^+ forms.[390] Crystalline titanium phosphate also exhibits a unidimensional intercrystalline swelling,[366] when amines are incorporated into the crystals either from the gaseous phase or from solution. The incorporation of amines leads to an increase in one lattice parameter only.[366]

Titanium phosphate has been used for the separation of radioactive Cs from strongly acidic nuclear-fuel reprocessing solutions,[395,396] to separations of Curie-level activities of ^{228}Th and ^{227}Ac from traces of ^{226}Ra,[397] and to the thin-layer chromatographic separation of Na from K.[398]

Titanium arsenate and antimonate. By mixing sodium arsenate solution with $TiCl_4$, glassy amorphous *titanium arsenate* with composition $Ti(HAsO_4)_2{\cdot}2{\cdot}5H_2O$ is formed[399] which has an exchange capacity of about 1 meq/g. The exchanger is highly selective towards Pb^{2+}, Cu^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Mn^{2+} and Cd^{2+} and can be used for the separation of Pb^{2+} from a series of bivalent metals as well for Ba–Mg, Ba–Ca and Ba–Sr separations.[399]

Crystalline titanium arsenate of composition $Ti(HAsO_4)_2{\cdot}H_2O$ is prepared by dissolving the freshly prepared amorphous titanium arsenate in 8*M* arsenic acid and subsequent refluxing for 45 hr.[400] The compound is hydrolysed considerably at $pH > 5$, so the total exchange capacity (5·8 meq/g) cannot be completely utilized.

Titanium antimonate is prepared by mixing $TiCl_4$ and $SbCl_5$ solutions and subsequently neutralizing with ammonia.[401] Amorphous products with Sb:Ti ratio ~1·0 and exchange capacity ~0·7 meq/g are obtained. The structure of the exchanger is built up from TiO_2 and Sb_2O_5, which are condensed together, giving the polymer



The hydrogen of the Sb-OH group is considered to be responsible for the cation-exchange capacity.[401] Separations such as Mg–Sr, Mg–Ca, Mg–Al, and Mn^{2+}–Al^{3+} have been achieved with this exchanger.[401]

Titanium molybdate and tungstate. Titanium molybdate is prepared by mixing $TiO(SO_4)_2$ or $TiCl_4$ solutions with an acidic solution of sodium molybdate. Amorphous products with Mo/Ti ratio ranging from 0·5 to 2·0 have exchange capacity between 0·8 and 1·6 meq/g. The capacity is substantially changed by heating the exchanger to 200°.[402] High selectivity of this exchanger towards Pb^{2+}, Ba^{2+}, Tl^{+} and K^{+} has been found and numerous separations such as Zn^{2+}–Pb^{2+}–Tl^{+}, Bi^{3+}–Pb^{2+}–Tl^{+},[402] Na–Rb, K–Cs, Ba–Ca and Na–Cs[403] have been achieved.

Titanium tungstate, prepared in a similar way to titanium molybdate, is an amorphous material which is highly stable towards mineral acids.[404] The exchange capacities vary between 0·42 and 0·76 meq/g depending upon the exchanger composition, and are higher for bivalent than univalent cations. Higher selectivity towards Ca^{2+} than other alkaline earth metal cations has been found, permitting the separation of Ca from Sr,Mg and Ba.[403,404] Other separations such as Na–Rb, K–Cs, Na–Cs,[403] and of Ga^{3+} from Fe^{3+}, Al^{3+} and In^{3+},[405] with this exchanger have been described. A paper impregnated with titanium tungstate is suitable for the separation of Au^{3+}, Tl^{3+}, Ag^{+}, Mo^{6+}, K^{+}, Rb^{+}, Cs^{+}, Ni^{2+}, Sb^{3+}, Bi^{3+}, Be^{2+} and Tl^{+} from numerous metal ions in aqueous and mixed-solvent media.[406]

Cerium salts

Cerium phosphate. When a solution of phosphoric acid is mixed with a solution containing a Ce(IV) salt a precipitate of cerium phosphate is formed, the composition, degree of crystallinity and structure of which are strongly dependent on experimental conditions such as precipitation medium, temperature, digestion time, PO_4/Ce ratio in the solution, rate and order of mixing, stirring *etc.* The products obtained may be divided into four groups: amorphous, microcrystalline, fibrous crystalline and crystalline cerium phosphate-sulphate.

The composition of the *amorphous* materials varies, with PO_4/Ce ratios between 1·03 and 1·95.[407,408] For some products an empirical formula $Ce_3(OH)_8(H_2PO_4)_4$ has been postulated.[409] If the precipitation is carried out in sulphuric acid media, the PO_4/Ce ratio decreases and the product contains 2–6% of sulphate.[407] The maximum exchange capacity of 2·9 meq/g[410] is totally lost on heating the exchanger to 200°.[410,411] The selectivity series for alkali metal cations follows the order of hydrated ionic radii, *ie.*, $Cs > Rb > K > Na > Li$.[409,410,412] Standard enthalpy changes have been determined for the Li–H, Na–H and K–H exchanges (+3·6, +3·1, −0·63 kJ/mole).[409]

The amorphous cerium phosphate also exhibits electron-exchange properties.[409] The oxidation of Mn^{2+} according to the equation

$$\begin{aligned} Ce_3^{IV}(OH)_8(H_2PO_4)_4 + 3Mn^{2+} \rightleftharpoons\ & Ce_3^{IV}(OH)_8Mn_3^{II}(HPO_4)_2(PO_4)_2 + 6H^+ \\ & \qquad\qquad\downarrow \\ & Ce^{III}(OH)_8Mn^{III}(HPO_4)_2(PO_4)_2 \end{aligned}$$

and the oxidation of I^- according to the equation

$$2Ce_3^{IV}(OH)_8(H_2PO_4)_4 + 9I^- \rightleftharpoons 2Ce_3^{III}(OH)_5(H_2PO_4)_4 + 3I_3^- + 6OH^-$$

have been observed.[409]

Microcrystalline cerium phosphate with a PO_4/Ce ratio of 1·5,[407,413] corresponding to the formula $(Ce{-}O{-}Ce)(HPO_4)_3{\cdot}H_2O$,[407] exhibits low ion-exchange capability.[412,413] Its affinity towards univalent cations increases in the order $Cs < Na < Ag$.[412]

Fibrous *crystalline* cerium phosphate, formulated as $Ce(HPO_4)_2{\cdot}H_2O$,[413] is stable towards hydrolysis[413,414] and exhibits a higher theoretical capacity (~5·2 meq/g) than the amorphous material. However, its capacity is lower at low pH (<3·3) than that of amorphous cerium phosphate. Similar behaviour has also been observed for zirconium and titanium phosphates and has been explained by the fact that in the amorphous materials the exchangeable hydrogen ions display a larger range of acidities than in the crystalline materials, so that some exchange may occur at lower pH values.[413]

Crystalline *cerium phosphate-sulphates* are obtained by precipitation from sulphuric acid solutions.[407] Products containing at least 0·75% w/w of sulphate exhibit their own crystal structure, which does not change till one HPO_4^{2-} group has been exchanged for an SO_4^{2-} group. Another crystal structure was found at higher SO_4^{2-} content up to a Ce:P:S ratio of 2:1:2.[415] These compounds may be formulated as $Ce_2O(HPO_4)_{3-x}(SO_4)_x \cdot 4H_2O$, where $0 < x < 1$. It is supposed that they possess a zeolytic structure, which is demonstrated by the fact that on Na^+ or Ag^+ exchange for H^+ no change in the crystal structure occurs.[412] The exchange capacity decreases with increasing SO_4^{2-} content[415] owing to the replacement of an active HPO_4^{2-} group for an inactive SO_4^{2-} group. However, products with Ce:P:S ratios up to 2:2:1 exhibit very good mechanical as well as ion-exchange properties. The selectivity towards various cations decreases in the order Na > Ag > Sr > Ba > Cs > Ca, the Be^{2+}, Co^{2+}, Fe^{3+} and Y^{3+} ions being not adsorbed at all.[415] It is concluded that only ions having an effective ionic radius $\lessdot 0{\cdot}6$ nm can enter the exchanger, which behaves as an ion-sieving material.

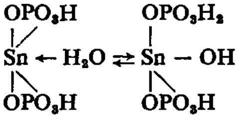
Cerium phosphates have been used for the column separations of Na from Cs and of Cs from Ba;[416,417] Li–Na–K, Ni–Ag–Tl and Co^{2+}–Eu^{3+}–Fe^{2+} separations have been carried out on a cellulose–cerium phosphate paper.[418] Fibrous cerium phosphate is suitable for preparing thin-layer membranes resistant to high temperature, ionizing radiation and oxidants.[419]

Cerium arsenate. Cerium arsenate is prepared by mixing a solution of cerium sulphate in sulphuric acid with arsenic acid and refluxing. A crystalline product of composition $Ce(HAsO_4)_2 \cdot 2H_2O$ is obtained, which loses one molecule of water at 60° and the second at 110°. A total exchange of Li^+ and Na^+ for H^+ has been achieved,[420] which was not the case with larger cations. The first interplanar distance increases with the degree of conversion into the Li^+ or Na^+ forms, similarly to the behaviour of other crystalline salts of this type. Hydrated cations enter the exchanger at low exchanger loading, whereas partly or totally dehydrated cations enter the exchanger at higher loading, and this is accompanied by selectivity reversal. The exchange isotherms show good reversibility for the Li^+–H^+ exchange, probably owing to the crystal structure of the starting and back-exchanged H^+ forms being the same.[420] However, small and remarkable hystereses were found for the total Na^+–H^+ and K^+–H^+ half-exchange.[420]

Stannic salts

Stannic phosphate. Stannic phosphate is prepared by mixing $SnCl_4$ solutions with NaH_2PO_4 solutions of different acidities.[421,422] Amorphous products with P/Sn ratio from 1·25[422] to 1·50[386] are highly stable towards ionizing radiation as well as in hydrothermal conditions.[422] Granular materials are obtained by mixing $Sn(SO_4)_2$ solution with concentrated phosphoric acid at 20°.[464] The ion-exchange capacity of stannic phosphate increases with increasing P/Sn ratio,[421] reaching maximum values between 1·2 and 1·44 meq/g,[386,422] and is lost on heating the exchanger.[422] The titration curves of this exchanger show a series of irregular kinks, indicating several dissociable hydrogen ions with a range of pK values.[422] The affinity for alkali metal cations follows the order Cs > Rb > K > Na > Li[422] and for the bivalent transition metals the order Cu > Zn > Ni > Co.[386] Irregularities were found in the alkaline earth metal series, where Ca^{2+} was preferred to Sr^{2+},[422] and for the adsorption of Zr^{4+}, where the K_d values did not depend upon the nitric acid concentration.[423,424] This behaviour of Zr^{4+} is explained either by the formation of a stable zirconium compound in the interior of the exchanger particles or by Zr exchange for Sn.[423,424]

Recently, crystalline stannic phosphate of composition $Sn(HPO_4)_2{\cdot}H_2O$ has been prepared by refluxing solutions containing $SnCl_4$, HNO_3 and H_3PO_4.[425] This exchanger is readily hydrolysed in alkaline solutions and loses its chemically bound water at a rather lower temperature (<350°) than the other crystalline phosphates of this type. The total exchange capacity for Na^+ corresponds to the stoichiometric formula. However, for the exchange of Li^+ a higher total capacity has been reached (7·9 meq/g), indicating probably the presence of more than two exchangeable hydrogen equivalents per formula weight of the exchanger. This is explained by the following tautomeric equilibrium in the solid:[425]



Stannic phosphate has found a wide range of useful separation applications, especially in the processing of radioactive effluents. Thus uranium can be separated from Sr,Cs and rare earths with a decontamination factor of $\sim 3{\cdot}10^3$,[424,426] as well as Sr and Cs from fission product solutions.[396,427] Complete separations such as K–Rb, Na–Cs, K–Cs, K–Na,[422,424] ^{89}Sr–^{137}Cs, ^{89}Sr–^{144}Ce, ^{137}Cs–^{144}Ce, ^{90}Sr–^{90}Y[428] have been described. Papers impregnated with stannic phosphate are suitable for chromatographic separation of a great number of cations.[429–432]

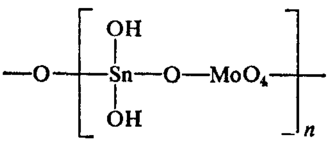
Stannic arsenate and antimonate. By mixing $SnCl_4$ solutions with Na_2HAsO_4[433] or H_3AsO_4,[434] amorphous *stannic arsenate* (Sn/As ~ 1·8) is formed. This material is stable in dilute acids and exhibits relatively high temperature stability.[433] The exchange capacity is between 0·79 and 0·94 meq/g, depending upon the As/Sn ratio in the solid. The distribution coefficients measured for a series of bi- and tervalent cations[433,434] show selectivity series corresponding to the order of ionic radii in the cases of alkaline earth metals, Al^{3+}, Ga^{3+} and In^{3+}. A disagreement found in the case of bivalent transition metals is explained by the decisive role of the solubility products of the corresponding arsenates of the metal ions in the adsorption process.[434]

Crystalline stannic arsenate is prepared either by refluxing the amorphous material with H_3AsO_4[434] or by refluxing solutions containing $SnCl_4$, HNO_3 and H_3AsO_4.[425] This material, of composition $Sn(HAsO_4)_2{\cdot}H_2O$,[425] is readily hydrolysed in alkaline media and exhibits ion-sieve properties, adsorbing only Li^+ and Na^+ ions from acid solutions. The exchange capacity found for Li^+ exceeds the formula capacity, which is explained similarly as in the case of crystalline stannic phosphate.[425]

A series of separations with stannic arsenate, such as Cu–Pb, Cu–Fe^{3+}, Fe^{2+}–Pb^{2+}, Fe^{2+}–Cu,$^{2+}$ Fe^{2+}–Fe^{3+},[433] Sr–Ba, Mg–Ba, Ca–Ba, Co^{2+}–Fe^{3+}, Al^{3+}–Fe^{3+}, Mn^{2+}–Fe^{3+}, Ca^{2+}–Fe^{3+}, Ni^{2+}–Fe^{3+}, Al–In and Mg–Al[434] has been described.

Stannic antimonate, prepared from $K_2H_2Sb_2O_7$ and $SnCl_4$ solutions, forms glass-like materials (Sb/Sn = 1:4–2:1) which are highly resistant towards mineral acids[435,436] and are suitable for use in column separation of alkali metal cations.

Stannic molybdate and tungstate. Stannic molybdate is prepared by mixing $SnCl_4$ with ammonium molybdate solutions.[437] Semitransparent amorphous granules with Sn:Mo ratio 1:1 and an exchange capacity of about 1·0 meq/g are obtained. The structure of this exchanger is tentatively postulated as



$$-\mathrm{O}-\left[\begin{matrix}\mathrm{OH}\\ |\\ -\mathrm{Sn}-\mathrm{O}-\mathrm{MoO_4}-\\ |\\ \mathrm{OH}\end{matrix}\right]_n-$$

The exchanger exhibits rather low stability towards hydrolysis (the Na^+ form being more stable than the H^+ form). High selectivity for Pb^{2+} ions has been found, which can be used for the separation of Pb^{2+} from a series of metal ions.[437]

Hard, semitransparent granules of *stannic tungstate* are prepared by mixing $SnCl_4$ with sodium tungstate solutions.[438] The product, with Sn/W ratio 1:3, is much more stable towards hydrolysis than stannic molybdate, and has an exchange capacity of ~0·58 meq/g which decreases on heating the exchanger to 100°. The selectivity for Co^{2+}, Ba^{2+}, Ni^{3+}, Pb^{2+}, Mn^{2+}, Cu^{2+} and Sr^{2+} ions has been established.[438] Papers impregnated with stannic tungstate are suitable for the separation of Zn^{2+}, Cd^{2+}, Au^{3+}, Ga^{3+}, Mg^{2+}, K^+, Rb^+, Cs^+ and Zr^{4+}.[431,439]

Other Acidic Salts

This group of ion-exchangers includes phosphates, polyphosphates and vanadates of tervalent and some bivalent cations, such as chromium, aluminium, iron, uranyl, alkaline earth metals, zinc, copper and tin.

Chromium phosphate is a polyfunctional gel-like radiation-resistant[440] cation-exchanger[441] with different PO_4/Cr ratios ranging from 0·6 to 1·0.[265] Empirical formulae such as $Cr_2O_2HPO_4$, $Cr_2O(HPO_4)_2$[265] and $CrPO_4$[441] have been proposed for these compounds. The maximum exchange capacity is 5·9 meq/g,[265,442] decreasing with increasing ionic radius of the ingoing ion.[265] The selectivities towards alkali and alkaline earth metal cations decrease in the orders $Na > K > Rb > Cs$ and $Ca \geqslant Sr > Ba$, respectively.[265] Separations of alkali metals and some transition metals such as K^+–Cs^+, Rb^+–Cs^+, Rb^+–Sr^{2+}, $Mn^{2+}Fe^{3+}$, Co^{2+}, –Fe^{3+}, Tc(IV)–Mo(VI) ,Sn^{2+}–In^{3+},[443] as well as the isolation of ^{59}Fe from Co,[442] have been described.

Chromium tripolyphosphate is prepared by mixing sodium tripolyphosphate with $CrCl_3$ solutions. Green glassy products with Cr/P ratio of 1:2·48 are obtained, exhibiting poor solubility in acids.[444] Their composition corresponds to the empirical formula $Cr_5(P_3O_{10})_3{\cdot}xH_2O$.[444] The exchange capacity for alkali metal cations is linearly dependent upon the pH of the external solution. The substance is highly selective towards alkali metal cations ($Cs > Rb > K > Na > H$), the uptake of bi-, ter- and quadrivalent cations being negligible.[444] A complete separation of Na, K, Rb and Cs has been achieved with this material, even in the presence of bi-, ter- and quadrivalent cations.[445,446] By evaporating $CrCl_3$ solution in phosphoric acid at 200–280°[447] another product, with composition $H_2CrP_3O_{10}{\cdot}2H_2O$, is formed, which is highly selective towards Ag^+.[447] The infrared spectra indicate that the water molecules are partly dissociated into H_3O^+ and OH^- groups.[448] The exchange of K^+ for H^+ led to the formation of an anhydrous compound, $K_2CrP_3O_{10}$.[447]

Aluminium and ferric triphosphates have been prepared with M/P ratios of 0·5–0·66 and can be used as selective ion-exchangers for K^+ ions within a limited pH range (2·5–6·0).[449] *Ferric pyrophosphate* $Fe_4(P_2O_7)_3$, has been studied for the adsorption of In^{3+}. It is noticeable that Fe^{3+} was displaced by In^{3+} ions during this process.[450]

Aluminium vanadate with composition $(Al_2O_3)_n(V_2O_5)_m(n/m = 2{\cdot}0\text{–}0{\cdot}5,\ m = 2\text{–}10)$ can be used as an ion-exchange membrane or may be sintered with a ceramic material without significant loss of exchange capability. The membranes operate efficiently up to 900°.[451]

Uranyl hydrogen phosphate ($UO_2HPO_4{\cdot}4H_2O$) and its salts with univalent and bivalent cations act as cation-exchangers, the exchange involving hydrogen (or M^+, M^{2+}) ions from the phosphate groups.[452,453] An unusual affinity series has been found for univalent cations, $NH_4 > Cs \sim Rb \sim K \gg Na$, which follows the series of increasing solubility products of the corresponding alkali metal uranyl phosphates.[454] High affinity for the ammonium ion is explained by the solubility product of ammonium uranyl phosphate having the lowest value.[454] On heating uranyl hydrogen phosphate to 300° a conversion into uranyl orthophosphate and liberation of the phosphoric acid occurs,[455] which causes substantial changes in the selectivity, bi-, ter- and quadrivalent cations being preferred. Na^+ can be separated from K^+, Rb^+ and Cs^+, but a complete separation of the alkali metals is impossible.[452] Separations of Co^{2+} from Zn^{2+}, Ce^{3+} from Cs^+, Co^{2+} from Cs^+ and Y^{3+} from Sr^{2+} have also been achieved with this exchanger.[452] For the adsorption of quadrivalent cations (Th^{4+}, Pu^{4+}, Zr^{4+}) on ammonium uranyl phosphate a precipitation mechanism has been found,[456,457] leading to the formation of insoluble phosphates of the type $(NH_4)_xH_yM^{IV}_{3-x-y}(PO_4)_{4-x-y}$, where $0 < x,y < 2$ and $(x + y) < 2$. Thus the formation of $NH_4M_2^{IV}(PO_4)_3$ was found on adsorption of Th^{4+} and Pu^{4+} and the formation of $Zr_3(PO_4)_4$ on adsorption of Zr^{4+}.[456,457]

A precipitation mechanism rather than ion-exchange has also been reported for other phosphates of bivalent metals, such as *calcium phosphate*,[458,459,460] *ammonium magnesium phosphate*,[461] *zinc phosphate*[462,463] and *copper phosphate*.[463]

Stannous polyphosphate exhibits electron-exchange properties,[360] reducing I_2, Fe^{3+} and Ag^+. The electron-exchange capacity varies between 0·44 and 0·59 meq/g.

Zusammenfassung—Eine ausführliche Literaturübersicht ist gegeben von hydratisierten Oxyden und sauren Salzen von vielwertigen Metallen die als Ionenaustauschsubstanzen anwendbar sind. Die Übersicht schliesst die Herstellung, Eigenschaften, Anwendbarkeit und Theorie von diesen Substanzen ein.

Résumé—Une revue complété est présenté sur les oxides hydratés et sels acides de métaux multivalents qui sont usés en qualité de matériaux échangeurs d'ions. La revue couvre la preparation, les qualités, usages et théorie de ces matériaux.

REFERENCES

1. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
2. I. S. C. Churms, *S. African Ind. Chemist*, 1965, **19**, 26, 48, 68, 87, 148.
3. E. A. Materova, F. A. Belinskaya, E. A. Militsina and P. A. Skabichevskii, *Ionnyi Obmen, Leningr. Gos. Univ.* 1965, 3.
4. M. Deak, *Magy. Kem. Lapja*, 1969, **24**, 316.
5. M. Abe and T. Ito, *Nippon Kagaku Zasshi*, 1965, **86**, 817.
6. R. Dutta and S. K. Baneryi, *Chem. Age India*, 1967, **18**, 513.
7. Ya. I. Korenman, *Tr. po Khim. i Khim. Tekhnol.*, 1964, 124.
8. N. F. Ermolenko and T. P. Karataeva, *Dokl. Akad. Nauk Belorussk. SSR*, 1965, **9**, 668.
9. F. Kepák, *Collection Czech. Chem. Commun.*, 1965, **30**, 1464.
10. L. Lindner, *AEC Accession* No. 13525, *Rept. No.* KFK-216.
11. R. J. Atkinson, A. M. Posner and J. P. Quirk, *J. Phys. Chem.*, 1967, **71**, 550.

12. L. Liepina and A. Ruplis, *Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser.*, 1965, 545.
13. H. H. Stamm and H. W. Kohlschütter, *J. Inorg. Nucl. Chem.*, 1965, **27**, 2103.
14. A. Lewandowski and S. Idzikowski, *Chem. Anal.* (Warsaw), 1966, **11**, 611.
15. A. Lewandowski, W. Czemplik and A. Dzik, *Zeszyty Nauk. Uniw. Poznaniu, Mat., Fiz., Chem.*, No. 3, 3 (1960).
16. A. K. Moulik, S. N. Chakravarti and S. K. Mokherjee, *J. Indian Chem. Soc.*, 1970, **47**, 149.
17. S. Shimomura, Y. Nishimara, Y. Fukumoto and Y. Tanase, *Eisei Kagaku*, 1969, **15**, 84.
18. D. Kyriacou, *Surface Soil*, 1967, **8**, 370.
19. E. D. Reyes and J. J. Jurinak, *Soil Sci. Soc. Amr. Proc.* 1967, **31**, 637.
20. W. M. McLellon, Univ. Microfilms (Ann Arbor, Mich.) Order No. 67-12, 840, pp. 376 (1967).
21. G. A. Solomin and T. O. Goncharova, *Gidrokhim. Mater.*, 1968, **48**, 143.
22. V. T. Chuiko and A. I. Gavrilyuk, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, 1967, No. 9, 57.
23. B. Holynska, *Rudy Metale Niezelazne*, 1965, **10**, 54.
24. E. Upor, A. Ronai and M. Gorbicz, *Acta Chim. Acad. Sci. Hung.*, 1969, **61**, 1.
25. W. Schulze and M. Scheffler, *Z. Anal. Chem.*, 1967, **226**, 395.
26. *Idem, ibid.*, 1967, **229**, 161.
27. K. Svoboda and B. Mudrová, *Radiochim. Acta*, 1967, **7**, 57.
28. V. T. Chuiko and A. I. Gavrilyuk, *Visn. L'viv. Derzh. Univ., Ser. Khim.*, 1969, No. 11, 49–54.
29. F. Kepák, *Czech. Patent* 131,067 (1969).
30. *Idem, Czech. Patent* 121,367 (1966).
31. G. K. Korpi, Dissertation, Stanford Univ., 1965, No. 65–9444, *Dissertation Abstr.* 1965, **26**, 1367.
32. R. H. Radzilowski, Y. F. Yao and J. Kummer, *Appl. Phys.*, 1969, **40**, 4716.
33. S. Mukai, T. Wakamatsu, M. Ichidate and N. Narazaki, *Suiyokai-Shi*, 1969, **16**, 635.
34. S. C. Churms, *J. S. Afr. Chem. Inst.*, 1966, **19**, 98.
35. L. Jacimovic, V. Veljkovic and N. Ajdacic, *Radiochim. Acta*, 1969, **12**, 49.
36. S. C. Churms, *J. S. Afr. Chem. Inst.*, 1966, **19**, 108.
37. Y. Belot, C. Gailledreau and R. Rzekiecki, *Health Phys.*, 1966, **12**, 811.
38. K. C. Williams, J. L. Daniel, W. J. Thompson, R. I. Kaplan and R. W. Maatman, *J. Phys. Chem.*, 1965, **69**, 250.
39. J. Schnekenburger, *Pharm. Ztg.*, 1968, **113**, 1606.
40. S. Tustanowski, *J. Chromatog.*, 1967, **31**, 270.
41. A. Kulesza, *Nukleonika* 1969, **14**, 216.
42. M. P. Volynec and A. N. Ermakov, *Uspekhi Khim.*, 1970, **39**, 934.
43. F. Girardi, R. Pietra and E. Sabbioni, *J. Radioanal. Chem.* 1970, **5**, 141.
44. T. Ito and T. Kenjo, *Nippon Kagaku Zasshi*, 1968, **89**, 162.
45. F. Burriel Marti and M. E. Garcia Clavel, *Anales Real Soc. Espan. Fis. Quim. (Madrid), Ser. B*, 1965, **61**, 945.
46. W. Dyck, *Can. J. Chem.* 1968, **46**, 1441.
47. W. Bannasch and H. H. Stamm, *AEC Accession No.* 15670, *Rept. No.* KFK-233.
48. V. Marková and F. Vydra, *Chem. Listy*, 1966, **60**, 860.
49. K. Unger and F. Vydra, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1075.
50. G. A. Parks, *Chem. Rev.*, 1965, **65**, 185.
51. J. Doležal, J. Horáček, J. Šrámek and Z. Šulcek, *Mikrochim. Acta*, 1966, 38.
52. R. L. Burwell, R. G. Pearson, G. L. Haller, P. B. Tjok and S. P. Chock, *Inorg. Chem.* 1965, **4**, 1123.
53. A. A. Agzamkhodzhaev, L. T. Zhuravlev and A. V. Kiselev, *Izv. AN SSSR, Ser. Khim.*, 1968 **6**, 1186.
54. N. G. Roslyakova and V. B. Aleskovskii, *Zh. Prikl. Khim.*, 1966, **39**, 795.
55. H. Otouma and H. Ukihashi, *Bull. Chem. Soc. Japan*, 1965, **38**, 1634.
56. R. Yu. Sheinfain and I. E. Neimark, *Kinetika i Kataliz*, 1967, **8**, 443.
57. N. Dimov, *Godishnik Nauchnoizsled. Inst. Neftoprerab. Neftokhim.*, 1966, **5**, 167.
58. E. M. Flanigen and R. W. Grose, *U.S. Patent*, 3,494,874 (1970).
59. M. R. Zaki and I. Abd-El-Moneim, *Z. Anorg. Allgem. Chem.* 1968, **360**, 208; 1969, **365**, 325.
60. O. P. Stas, R. Yu. Sheinfain and I. E. Neimark, *Kolloid Zh.*, 1970, **32**, 104.
61. N. V. Akshinskaya, V. Yu. Davydov, A. V. Kiselev and Yu. S. Nikitin, *ibid.*, 1966, **28**, 3.
62. V. M. Chertov and I. E. Neimark, *Ukr. Khim. Zh.*, 1969, **35**, 499.
63. R. E. Majors and L. B. Rogers, *Anal. Chem.*, 1969 **41**, 1052.
64. *Idem, ibid.*, 1969, **41**, 1058.
65. I. B. Slinjakova, G. B. Budkevich and I. E. Neimark, *Kolloid. Zh.*, 1965, **27**, 758.
66. R. Yu. Sheinfain and O. P. Stas, *Zh. Prikl. Khim. (Leningrad)*, 1969, **42**, 2363.
67. K. Unger and K. Berg, *Z. Naturforsch. B*, 1969, **24**, 454.

68. A. M. Kuliev and E. V. Grigoryna, *Azerb. Neft. Khoz.*, 1964, **43**, 46.
69. E. K. Hurley, M. F. Burke, J. E. Heveran and L. B. Rogers, *Separation Sci.*, 1967, **2**, 275.
70. M. F. Burke, A. K. Moreland and L. B. Rogers, *ibid.*, 1968, **3**, 107.
71. H. W. Kohlschütter, A. Risch, K. Unger and K. Vogel, *Ber. Bunsenges. Physik. Chem.*, 1965, **69**, 849.
72. I. P. Alekseeva and A. P. Dushina, *Kolloid. Zh.*, 1969, **31**, 483.
73. H. Ti Tien, *J. Phys. Chem.*, 1965, **69**, 350.
74. R. W. Maatman, *ibid.*, 1965, **69**, 3196.
75. D. Michel, *Z. Naturforsch.*, *A* 1967, **22**, 1751.
76. E. G. Nekrasova, I. V. Zhilenkov and V. M. Fedorov, *Zh. Strukt. Khim*, 1968, **9**, 406.
77. G. A. Galkin, A. V. Kiselev and V. I. Lygin, *Zh. Fiz. Khim.*, 1968, **42**, 1470.
78. J. Uytterhoeven, M. Sleex and J. J. Fripiat, *Bull. Soc. Chim. France*, 1965, 1800.
79. R. M. Umarkhodzhaev, N. M. Ievskaya, L. V. Matveets and V. A. Gromov, *Zh. Fiz. Khim.*, 1968, **42**, 2141.
80. K. A. Suprunenko, V. V. Strelko and A. M. Kabakhi, *Teor. Eksp. Khim.*, 1969, **5**, 353.
81. L. F. Kirichenko and Z. Z. Vysotskii, *Dokl. Akad. Nauk SSSR*, 1967, **175**, 635.
82. V. M. Chertov, D. B. Dzhambaeva and I. E. Neimark, *Ukr. Khim. Zh.*, 1965, **31**, 1149.
83. L. F. Kirichenko, V. M. Chertov, Z. Z. Vysotskii and D. N. Strazhesko, *Dokl. Akad. Nauk SSSR*, 1965, **164**, 618.
84. J. Uytterhoeven, J. Andre and J. J. Fripiat, *Bull. Soc. Chim. France*, 1965, 1804.
85. S. I. Kol'tsov and V. B. Aleskovskii, *Zh. Fiz. Khim.*, 1968, **42**, 1210.
86. S. S. Jorgensen, *Acta Chem. Scand.* 1968 **22**, 335.
87. F. Vydra, *Anal. Chim. Acta*, 1967, **38**, 201.
88. H. W. Kohlschütter and L. Schaefer, *Z. Anal. Chem.*, 1969, **245**, 129.
89. C. E. Lewis, *Ph.D. Thesis*, University of Essex (1968).
90. L. H. Allen and E. Matijevic, *J. Colloid Interface Sci.*, 1970, **33**, 421.
91. L. F. Kirichenko, D. N. Strazhesko and G. F. Yankovskaya, *Ukr. Khim. Zh.*, 1965, **31**, 160.
92. C. Konečný, *Nuclear Res. Inst.*, *Czech. Acad. Sci.*, *Report No.* UJV 2119-Ch (1969).
93. V. V. Strelko, D. N. Strazhesko, N. I. Soloshenko, S. K. Rubanik and A. A. Baran, *Dokl. Akad. Nauk SSSR*, 1969, **186**, 1362.
94. S. K. Rubanik, A. A. Baran, D. N. Strazhesko and V. V. Strelko, *Teor. Eksp. Khim.*, 1969, **5**, 361.
95. R. W. Dalton, J. L. McClanahan and R. W. Maatman, *J. Colloid Sci.*, 1962, **17**, 207.
96. N. S. Mal'ceva and Z. Czeglowski, *Radiokhimiya*, 1970, **12**, 622.
97. W. Bannasch, *AEC Accession No.* 41562, *Rept. No.* KFK-215 (1964).
98. R. W. Maatman and A. Kramer, *J. Phys. Chem.*, 1968, **72**, 104.
99. O. Papavassiliou, *Chim. Chronika (Athens)* 1966, **31**, 17.
100. M. Sakanoue and M. Abe, *Radioisotopes (Tokyo)*, 1967, **16**, 645.
101. I. G. Syrkina and Yu. M. Martinov, *Zh. Fiz. Khim.*, 1967, **41**, 3140.
102. F. Vydra and V. Marková, *Collection Czech. Chem. Commun.*, 1966, **31**, 1398.
103. V. V. Strelko, B. M. Mitsiyuk, A. I. Kazantseva and Z. Z. Vysotskii, *Dokl. Akad. Nauk SSSR*, 1968, **179**, 1392.
104. M. F. Smirnova, A. P. Doshina and V. B. Aleskovskii, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1968, **4**, 248.
105. F. Vydra and V. Marková, *Collection Czech. Chem. Commun.*, 1967, **32**, 1614.
106. N. N. Tikhomirova and I. V. Nikolaeva, *Metody Issled. Katal. Reakts.*, *Akad. Nauk SSSR, Sib. Otd.*, *Inst. Katal.*, 1965, **3**, 82.
107. A. L. Kondrasheva, A. P. Dushina and V. B. Aleskovskii, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1969 **5**, 2155.
108. Yu. M. Martynov and I. G. Syrkina, *Zh. Prikl. Khim. (Leningrad)*, 1967, **40**, 1374.
109. A. V. Davidov and I. N. Marov, *sbornik Soosashdeniie i adsorbcia radioaktivnikh elementov*, Nauka, Moscow, 1965.
110. R. Caletka, *Collection Czech. Chem. Commun.*, in the press.
111. O. Ch. Papavasileou, *Chim. Chronika (Athens)* 1964, **29**, 267.
112. J. Rais and M. Kyrš, *Collection Czech. Chem. Commun.*, 1965, **30**, 983.
113. R. Caletka, *Radiokhimiya*, 1970, **12**, 448.
114. R. Caletka and T. D. Zaitseva, *ibid.*, 1969, **11**, 510.
115. J. Krtil and Z. Kolařík, *Collection Czech. Chem. Commun.*, 1965, **30**, 824.
116. A. P. Dushina and V. B. Aleskovskii, *Zh. Obshch. Khim.* 1968, **38**, 1419.
117. A. S. Plachinda, V. M. Chertov and I. E. Neimark, *Ukr. Khim. Zh.*, 1965, **31**, 567.
118. F. Vydra and J. Galba, *Collection Czech. Chem. Commun.*, 1969, **34**, 3471.
119. *Idem*, *ibid.*, 1967, **32**, 3530.
120. *Idem*, *Z. Anal. Chem.*, 1968, **235**, 166.

121. A. V. Davydov, I. N. Marov and P. N. Palei, *Colloq. Intern. Centre Natl. Rech. Sci. (Paris).* 1966, No. 154, 181.
122. R. Caletka, *Radiokhimiya*, 1970, **12**, 554.
123. *Idem, ibid.*, 1970, **12**, 558.
124. R. W. Maatman, A. Geertsema, H. Verhage, G. Baas and M. Du Mez, *J. Phys. Chem.*, 1968, **72**, 97.
125. R. Caletka, *Nuclear Res. Inst., Czech. Acad. Sci., Report No.* UJV 2264-Ch (1969).
126. *Idem, Radiochem. Radioanal. Letters*, 1969, **2**, 139.
127. *Idem, Collection Czech. Chem. Commun.*, in the press.
128. *Idem, ibid.*, in the press.
129. N. S. Mal'tseva and Z. Szeglowski, *Joint Inst. Nucl. Res., Dubna, USSR, Report* JINR P/12-4104 (1968).
130. J. Horski, *Inst. Nucl. Res. (Warsaw), Rept. No.* 636 (1965).
131. R. Otto and P. Hecht, *Atompraxis*, 1967, **13**, 27.
132. F. Vydra and V. Marková, *Collection Czech. Chem. Commun.*, 1965, **30**, 2382.
133. T. D. Ionescu and G. Tudorache, *Bul. Inst. Politeh. "Gheorge Gheorghiu-Dej", (Bucuresti)*, 1967, **29**, 67.
134. K. R. Kar and S. Singh, *Mikrochim. Acta*, 1970, 279.
135. R. Caletka and T. D. Zaitseva, *Zh. Analit. Khim.*, 1970, **25**, 82.
136. M. Rodriguez Parra, A. Uriarte Hueda and B. Lopez Perez, *An. Quim.*, 1968, **64**, 83.
137. Z. Šulcek, J. Kremer and J. Doležal, *Collection Czech. Chem. Commun.*, 1969, **34**, 1720.
138. R. Caletka, Private communication.
139. J. Doležal, J. Petřeková and Z. Šulcek, *Mikrochim. Acta*, 1966, 248.
140. V. I. Spitsyn, R. A. Dyachkova and A. M. Kamenskaya, *Dokl. Akad. Nauk SSSR*, 1969, **184**, 379.
141. M. Sakanoue and M. Abe, *Radioisotopes (Tokyo)*, 1967, **16**, 645.
142. R. Caletka and V. Knobloch, *Collection Czech. Chem. Commun.*, in press.
143. M. Rodriguez Parra, A. Uriarte Hueda and B. Lopez Perez, *C. R. Colloq. Fr.-Espagnol Trait. Combust. Irradies, 1st*, 1967, 201.
144. *Idem, An. Real. Soc. Espan. Fis. Quim., Ser. B*, 1966, **62**, 1275.
145. G. E. Jonauer and R. C. Johnston, *Anal. Chem.*, 1966, **38**, 786.
146. R. V. Bogdanov and A. O. Pyalling, *Vestn. Leningrad. Univ., Fiz., Khim.*, 1969, 160.
147. M. Lesigang-Buchtela, *Mikrochim. Acta*, 1969, 1027.
148. N. F. Ermolenko, V. V. Sviridov and G. A. Popkovich, *Kolloid. Zh.*, 1969, **31**, 190.
149. G. Siclet, J. Lenoir and Ch. Eyraud, *Bull. Soc. Chim. France*, 1966, 2995.
150. M. Okada, T. Shirasaki and K. Morikawa, *Shokubai (Tokyo)*, 1967, **9**, 171.
151. M. Okada, *ibid.*, 1967, **9**, 2.
152. Th. F. Tadros and J. Lyklema, *J. Electroanal. Chem. Interfacial Electrochem.*, 1968, **17**, 267.
153. B. J. Hathaway and C. E. Lewis, *J. Chem. Soc. A*, 1969, 2295.
154. *Idem, ibid.*, 1969, 1176.
155. *Idem, ibid.*, 1969, 1183.
156. *Idem, Chem. Commun.*, 1967, 504.
157. G. M. Popovich, E. V. Lunina, V. B. Golubev, V. B. Evdokimov and L. T. Bugaenko, *Vestn. Mosk. Univ., Khim.*, 1968, 94.
158. J. D. Donaldson and M. J. Fuller, *J. Inorg. Nucl. Chem.* 1968, **30**, 1083.
159. *Idem, Ibid.*, 1970, **32**, 1703.
160. J. D. Donaldson, M. J. Fuller and J. W. Price, *ibid.*, 1968, **30**, 2841.
161. H. Nishida, *Bunseki Kagaku*, 1965, **14**, 473.
162. I. N. Makatova and A. I. Mun, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* 1969, **19**, 74.
163. C. Heitner-Wirguin and A. Albu-Yaron, *J. Appl. Chem. (London)*, 1965, **15**, 445.
164. *Idem, J. Inorg. Nucl. Chem.* 1966, **28**, 2379.
165. *Idem, Belg. Patent* 1965, 668, 010.
166. D. Vivien, J. Livage and Ch. Mazieres, *J. Chim. Phys. Physicochim. Biol.* 1970, **67**, 199.
167. Yu. Ya. Bobyrenko, Yu. D. Dolmatov and M. I. Bragina, *Zh. Prikl. Khim. (Leningrad)*, 1970, **43**, 1152.
168. Yu. D. Dolmatov and A. I. Sheinkman, *ibid.*, 1970, **43**, 249.
169. E. Schiewer and H. W. Levi, *Radiochem. Conf., Abstr. Pap., Bratislava* (1966), p. 20.
170. H. W. Levi and E. Schiewer, *Radiochim. Acta*, 1966, **5**, 126.
171. I. V. Riskin and T. Velikoslavinskaya, *Zh. Prikl. Khim. (Leningrad)*, 1969, **42**, 1400.
172. H. W. Levi and E. Schiewer, *Radiochim. Acta*, 1968, **9**, 160.
173. *Idem, ibid.*, 1970, **14**, 43.
174. J. Kennedy, J. W. Peckett and R. Perkins, *AERE Report No.* R 4516 (1964).

175. *French Patent* 1,446,245 (1966).
176. N. J. Keen, *J. Brit. Nucl. Energy Soc.*, 1968, **7**, 178.
177. K. Sakodinski and M. Lederer, *J. Chromatog.*, 1965, **20**, 358.
178. V. I. Plotnikov and E. G. Gibova, *Izv. Akad. Nauk Kaz. SSR, Ser. Fiz.-Mat.* 1967, **5**, 58.
179. V. I. Plotnikov and V. L. Kochetkov, *ibid.*, 1967, **5**, 66.
180. *Idem, ibid.*, 1967, **5**, 57.
181. R. Sh. Mikhail and R. B. Fahim, *J. Appl. Chem.* (*London*), 1967, **17**, 147.
182. D. R. Vissers, *J. Phys. Chem.*, 1969, **73**, 1953.
183. K. S. Rajan and A. J. Casolo, *U.S. Patent* 3,479,266 (1969).
184. J. I. Bergman, D. E. Anthes and R. S. Braman, *U.S. Patent* 3,463,713 (1969).
185. K. S. Rajan, J. A. Hunter, W. S. Gillam and H. E. Podall, *U.S. Office Saline Water Res. Develop. Progr. Repl.* No. 328 (1968).
186. K. S. Rajan, D. B. Boies, A. J. Casolo and J. I. Bregman, *Desalination*, 1966, **1**, 231.
187. V. V. Vol'khin, E. I. Ponomarev and V. L. Zolotavin, *Ivz. Akad. Nauk SSSR, Neorgan. Mater.* 1965, **1**, 1573.
188. D. Naumann, *German* (*East*) *Patent* 40952 (1965).
189. L. M. Zaitsev, *Zh. Neorgan. Khim.*, 1966, **11**, 1684.
190. A. Clearfield, *Rev. Pure Appl. Chem.*, 1964, **14**, 91.
191. *Idem.*, *Inorg. Chem.*, 1964, **3**, 146.
192. K. M. Pant, *J. Indian Chem. Soc.*, 1969, **46**, 541.
193. J. Belloni-Cofler and D. Pavlov, *J. Chim. Phys.*, 1965, **62**, 458.
194. G. W. Smith and T. Salman, *Can. Met. Quart.*, 1966, **5**, 93.
195. D. Britz and G. H. Nancollas, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3861.
196. G. H. Nancollas and R. Paterson, *ibid.*, 1967, **29**, 565.
197. G. H. Nancollas and D. S. Reid, *ibid.*, 1969, **31**, 213.
198. A. Ruvarac, "*Boris Kidrich*" *Inst. Nucl. Sci. Rept.* IBK-560 (1967).
199. D. R. Vissers, *J. Phys. Chem.*, 1968, **72**, 3236.
200. D. R. Vissers, R. G. Wymer and K. A. Kraus, *U.S. Office Saline Water Res. Develop. Progr. Rept.* No. 302 (1968).
201. A. J. Shor, K. A. Kraus, W. T. Smith Jr, and J. S. Johnson Jr., *J. Phys. Chem.* 1968, **72**, 2200.
202. A. E. Marcinkowsky, K. A. Kraus, H. O. Phillips, J. S. Johnson and A. J. Shor, *J. Am. Chem. Soc.*, 1966, **88**, 5744.
203. K. A. Kraus, A. J. Shor and J. S. Johnson Jr., *Desalination*, 1967, **2**, 243.
204. S. Tustanowski, *J. Chromatog.*, 1967, **31**, 268.
205. A. I. Novikov and I. A. Starovoit, *Radiokhimiya*, 1969, **11**, 339.
206. A. I. Novikov, V. I. Ruzankin and V. S. Dedova, *ibid.*, 1969, **11**, 347.
207. V. I. Plotnikov and V. I. Kochetkov, *Izv. Akad. Nauk Kaz. SSR, Ser. Fiz.-Mat.*, 1967, **5**, 53.
208. V. I. Plotnikov, V. P. Novikov and M. M. Novikov, *ibid.*, 1967, **5**, 90.
209. L. Kosta, V. Ravnik and M. Levstek, *Radiochim. Acta*, 1970, **14**, 143.
210. B. Sansoni, R. Winkler and K. Starke, *Angew. Chem.*, 1966, **78**, 645.
211. C. Bigliocca, F. Girardi, J. Pauly and E. Sabbioni, *Anal. Chem.*, 1967, **39**, 1634.
212. A. Kozawa, *J. Electrochem. Soc.* 1959, **106**, 552.
213. V. V. Vol'khin and G. V. Leont'eva, *Izv. Akad. Nauk. SSSR, Neorgan. Mater.*, 1969, **5**, 1224.
214. G. V. Leont'eva and V. V. Vol'khin, *ibid.*, 1968, **4**, 728.
215. N. I. Lagidze, D. I. Dzhaparidze and L. N. Dzhaparidze, *Soobshch. Akad. Nauk. Gruz. SSR*, **53**, 585 (1969).
216. P. Benson, W. B. Price and F. L. Tye, *Electrochem. Technol.*, 1967, **5**, 517.
217. H. S. Posselt, F. J. Anderson and W. J. Weber, *Environ. Sci. Technol.*, 1968, **2**, 1087.
218. Yu. V. Egorov and B. N. Khrustalev, *Tr. Ural. Politekh. Inst.*, 1966, No. 148, 93.
219. M. A. Malati, A. A. Yousef and M. A. Arafa, *Chem. Ind.* (*London*), 1969, 459.
220. S. Meloni and A. Brandone, *Radiochim. Acta*, 1968, **10**, 97.
221. *Idem*, *Intern. J. Appl. Rad. Isotopes*, 1968, **19**, 164.
222. A. P. Tyutrina, B. P. Zhagin and V. G. Bakhurov, *At. Energ.* (*USSR*), 1965, **18**, 487.
223. T. Momma and K. Iwashima, *Radioisotopes* (*Tokyo*), 1967, **16**, 68.
224. A. J. Shuckrow, *Dissertation Abstr.* B, 1967, **28**, 1555.
225. M. Abe and T. Ito, *Bull. Chem. Soc. Japan*, 1968, **41**, 2366.
226. *Idem*, *ibid.*, 1968, **41**, 333.
227. B. G. Novikov, F. A. Belinskaya and E. A. Materova, *Véstn. Leningrad. Univ., Fiz., Khim.*, 1969, 97.
228. J. Lefebvre, *Compt. Rend.* 1965, **260**, 5575.
229. *Idem*, *French Patent* 1, 470, 347 (1967).
230. L. H. Baetslé and D. Huys, *J. Inorg. Nucl. Chem.*, 1968, **30**, 639.

231. J. Lefebvre and F. Gaymard, *Compt. Rend.*, 1965, **260**, 6911.
232. B. G. Novikov, T. G. Belicheva, F. A. Belinskaya and E. A. Materova, *Vestn. Leningrad. Univ., Fiz., Khim.*, 1969, 110.
233. M. Abe, *Kogyo Kagaku Zasshi*, 1967, **70**, 2226.
234. Ch. Aubertin and J. Lefebvre, *French Patent* 1,469,088 (1967).
235. J. M. Colin and J. Lefebvre, *Compt. Rend. Acad. Sci. (Paris), Ser. C*, 1969, **268**, 1760.
236. S. Cahuzac and J. Lefebvre, *ibid.*, 1968, **267**, 1127.
237. *Idem.*, *Bull. Soc. Chim. France*, 1969, 771.
238. M. Abe, *Bull. Chem. Soc. Japan*, 1969, **42**, 2683.
239. C. Konečný and V. Kouřím, *Radiochem. Radioanal. Lett.*, 1969, **2**, 47.
240. M. Abe and T. Ito, *Nippon Kagaku Zasshi*, 1966, **87**, 1174.
241. *Idem*, *ibid.*, 1965, **86**, 1259.
242. L. H. Baetslé, V. van Deyck, D. Huys and A. Geury, *Repl. EUR* 2497e (Euratom, Brussels 1965).
243. M. Abe and T. Ito, *Bull. Chem. Soc. Japan*, 1967, **40**, 1013.
244. Ch. Aubertin, J. Lefebvre, G. Galaud and J. Prospert, *U.S. Patent* 3,399,030 (1968).
245. L. H. Baetslé and D. Huys, *36th Intern. Congr. Industrial Chemistry*, Paper No. 12–14, Brussels 1966.
246. F. Girardi, R. Pietra and E. Sabbioni, *Nat. Bur. Stand. Spec. Publ.*, No. 312,639 (1969).
247. T. Ito and M. Abe, *Denki Kagaku*, 1965, **33**, 175.
248. L. H. Baetslé and D. Huys, *Belg. Patent* 649,746 (1964).
249. *French Patent* 1,438,742 (1966).
250. T. Ito and M. Abe, *Bull. Chem. Soc. Japan*, 1961, **34**, 1736.
251. R. F. Brigewich and R. A. Kuznetsov, *Radiokhimiya*, 1967, **9**, 693.
252. E. A. Materova, F. A. Belinskaya and E. A. Militsina, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1969, **5**, 1943.
253. F. A. Belinskaya, E. A. Materova, O. P. Shuvalova, L. A. Karhanova and O. I. Bulaeva, *Ionnyi Obmen, Leningr. Gos. Univ.*, 1965, 43.
254. V. A. Shichko and E. S. Boichinova, *Zh. Prikl. Khim. (Leningrad)*, 1968, **41**, 526.
255. Yu. I. Sukharev and Yu. V. Egorov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1969, **5**, 2159.
256. Yu. V. Egorov, Yu. I. Sukharev, A. S Lyubimov and E. I. Krylov, *ibid.*, 1967, **3**, 1210.
257. Yu. I. Sukharev and Yu. V. Egorov, *ibid.*, 1968, **4**, 996.
258. B. E. Chidley, F. L. Parker and E. A. Talbot, *AERE Repl.* No. R5220 (1966).
259. *French Patent* 1,486,949 (1967).
260. K. A. Kraus, *U.S. Patent* 3,332,737 (1967).
261. L. Szirtes and L. Zsinka, *Magy. Kem. Lapja*, 1966, **21**, 465.
262. V. F. Tikavyi and L. I. Tsukorova, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1965, **1**, 108.
263. K. B. Zaborénko, L. Szirtes and L. Zsinka, *Vestn. Mosk. Univ. Khim.* 1968, **23**, 59.
264. V. F. Tikavyi and V. D. Komarov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1969, **5**, 180.
265. L. Szirtes, L. Zsinka, K. B. Zaborenko and B. Z. Iofa, *Acta Chim. Acad. Sci. Hung.*, 1967, **54**, 215.
266. V. D. Komarov and V. F. Tikavyi, *Vestsi Akad. Navuk Belorusk. SSR, Ser. Khim. Navuk*, 1968, 19.
267. J. Prospert, *Comm. Energie At. (France), Rappt.* CEA-R 2835 (1966).
268. L. M. Sharygin, A. A. Pospelov and V. G. Chukhlantsev, *Radiokhimiya*, 1969, **11**, 568.
269. *Idem*, *ibid.*, 1965, **7**, 744.
270. V. I. Savel'eva and V. A. Minaev, *Tr. Mosk. Khim. Tekhnol. Inst.*, 1963, No, 43, 82.
271. G. H. Nancollas and V. Pekárek, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1409.
272. S. Ahrland, A. Oskarsson and A. Niklasson, *ibid.*, 1970, **32**, 2069.
273. J. Piret, *British Patent* 1,070,932 (1967).
274. J. A. Stynes and A. Clearfield, *U.S. Patent* 3,416,884 (1968).
275. A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
276. G. Alberti and E. Torracca, *ibid.*, 1968, **30**, 317.
277. A. Clearfield, R. H. Blessing and J. A. Stynes, *ibid.*, 1968, **30**, 2249.
278. F. Mounier and L. Winand, *Bull. Soc. Chim. France*, 1968, 1829.
279. L. Zsinka and L. Zsirtes, *Magy. Kem. Foly*, 1968, **74**, 258.
280. Yu. V. Egorov, *Radiokhimiya*, 1967, **9**, 374.
281. G. Garbauskas and V. I. Shamaev, *Zh. Neorgan. Khim.*, 1970, **15**, 33.
282. S. Ahrland and J. Albertsson, *Acta Chem. Scand.*, 1969, **23**, 1446.
283. A. Clearfield and S. D. Smith, *J. Colloid. Interface Sci.*, 1968, **28**, 325.
284. J. Albertsson, *Acta Chem. Scand.*, 1966, **20**, 1689.
285. L. Sedláková and V. Pekárek, *J. Less-Common Metals*, 1966, **10**, 130.

286. A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
287. *Idem*, *J. Inorg. Nucl. Chem.*, 1968, **30**, 327.
288. G. D. Smith, *Thesis*, Ohio Univ. Athens, Ohio, 1968.
289. V. Veselý, V. Pekárek and Z. Urbanec, *5th Radiochemical Conference*, Zvikov-Castle, Czechoslovakia, 1969.
290. V. Veselý, V. Pekárek and A. Ruvarac, *Bull. Soc. Chim. France*, 1968, 1832.
291. E. P. Horwitz, *J. Inorg. Nucl. Chem.*,1966, **28**, 1469.
292. S. Ahrland and J. Albertsson, *Acta Chem. Scand.* 1964, **18**, 1861.
293. A. Ruvarac and V. Veselý, *J. Inorg. Nucl. Chem.* 1970, **32**, 3939.
294. A. Clearfield and J. R. Thomas, *Inorg. Nucl. Chem. Lett.* 1969, **5**, 775.
295. A. A. Balandin, A. I. Kukina, V. I. Lygin and N. E. Malenberg, *Teor. Eksp. Khim.*, 1967, **3**, 561.
296. G. Alberti, E. Torracca and A. Conte, *J. Inorg. Nucl. Chem.*, 1966, **28**, 607.
297. G. Alberti, A. Conte and E. Torracca, *ibid.*, 1966, **28**, 225.
298. S. Ahrland, J. Albertsson, A. Alnas, S. Hemmingsson and L. Kullberg, *Acta Chem. Scand.*, 1967, **21**, 195.
299. V. F. Tikavyi and A. S. Zhukova, *Geterogennye Reaktsii i Reakts. Sposobnost (Minsk, Vyssh. Skola) Sb.*, 1964, 71.
300. V. Veselý, A. Ruvarac and L. Sedláková, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1101.
301. A. Ruvarac, *Thesis*, University of Belgrade (1970).
302. G. Alberti and P. Galli, *J. Inorg. Nucl. Chem.*, 1966, **28**, 658.
303. M. D. Hont and L. H. Baetslé, *Mededel. Koninkl. Vlaam. Acad. Wetenschap.*, *Belg.*, *Kl. Wetenschap*, 1965, **27**, 31.
304. A. V. Jadhav, Ch. L. Rao and C. J. Shahani, *Proc. Nucl. Radiat. Chem. Symp.*, *3rd* 1967, 436 (Bombay, India).
305. S. J. Harvie and G. H. Nancollas, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3923.
306. D. J. Murray and M. C. Fuerstenau, *ibid.*, 1968, **30**, 3325.
307. V. F. Tikavyi and V. D. Komarov, *Vestsi Acad. Navuk Belarusk. SSR*, *Ser. Khim. Navuk*, 1968, 41.
308. D. Cvjeticanin and N. Milic, *Bull. Boris Kidrich Inst. Nucl. Sci.* 1964, **15**, 73.
309. J. Y. Ollivier and T. Kikindai, *Compt. Rend. Acad. Sci.* (*Paris*), *Ser. C* 1966, **262**, 175.
310. E. Torracca, *J. Inorg. Nucl. Chem.* 1969, **31**, 1189.
311. A. Clearfield and A. S. Medina, *ibid.*, 1970, **32**, 2775.
312. A. Clearfield and J. Troup, *J. Phys. Chem.* 1970, **74**, 314.
313. S. J. Harvie and G. H. Nancollas, *J. Inorg. Nucl. Chem.*, 1968, **30**, 273.
314. A. Clearfield, W. L. Duax, A. S. Medina, G. D. Smith and J. R. Thomas, *J. Phys. Chem.*, 1969, **73**, 3424.
315. E. Michel and A. Weiss, *Z. Naturforsch. B*, 1965, **20**, 1307.
316. A. Clearfield and J. M. Troup, *J. Phys. Chem.*, 1970, **74**, 2578.
317. V. I. Savel'eva and E. B. Khlobystina, *Tr. Mosk. Khim.-Tekhnol. Inst.*, 1963, No. 43,89.
318. J. Barrett, J. A. W. Dalziel and M. K. Rahman, *Bull. Soc. Chim. France*, 1968, 1835.
319. V. Pekárek and V. Veselý, *Proc. Nucl. Fuel Reprocessing Comecon Conf.*, *Karlovy Vary*, 1968, p. 165.
320. V. Pekárek and S. Maryška, *Collection Czech. Chem. Commun.*, 1968, **33**, 1612.
321. A. Ruvarac, *Bull. Boris Kidrich Inst. Nucl. Sci.*, 1969, **20**, 33.
322. G. H. Nancollas and B. V. K. S. R. A. Tilak, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3643.
323. Ch. J. Wiedenheft, *ibid.*, 1969, **31**, 1859.
324. M. Lederer and L. Ossicini, *J. Chromatog.* 1966, **22**, 200.
325. E. Akatsu, R. Ono, K. Tsukuechi and H. Uchiyama, *J. Nucl. Sci. Technol.* (*Tokyo*), 1965, **2**, 141.
326. A. Ruvarac and A. Tolic, "*Boris Kidrich*" *Inst. Nucl. Sci. Rept.* IBK-452 (1966).
327. S. Ahrland and K. E. Holmberg, *Proc. Intern. Conf. Peaceful Uses At. Energy*, *3rd*, *Geneva*, 1964, **10**, 571.
328. J. Prospert, J. Lefebvre and A. Raggenbass, *Communaute Eur. Energ. At.-Euratom*, 1968, EUR-4075.
329. J. Lefebvre, J. Prospert and A. Raggenbass, *French Patent* 1,393,546 (1965).
330. *Idem*, *Fr. Addn.* 87,413 (1966).
331. L. H. Baetslé, D. van Deyck, D. Huys and A. Guery, *AEC Accession No.* 7613, *Rept. No.* BLG-267 (1964).
332. S. Ahrland, *French Patent* 1,473,361 (1967).
333. L. Zsinka and L. Szirtes, *Magy. Kem. Lapja*, 1966, **21**, 536.
334. H. J. Riedel, *Wiss.-Tech. Tagung Deut. Atomforums*, *2nd*, *Munich.* 1963, p. 252.

335. P. Batanero Sanchez, *Commis. Energ. At.* (*Fr.*) *Rapp.* 1969, CEA-R-3753.
336. K. Kimura, *Japan At. Energy Res. Inst.*, *Rept.* 1969, JAERI-1178,23.
337. I. Gal and N. Peric, *Mikrochim. Acta*, 1965, 251.
338. E. S. Boichinova and G. N. Strel'nikova, *Zh. Prikl. Khim.* (*Leningrad*), 1967, **40**, 1443.
339. K. V. Barsukova and G. N. Rodionova, *Radiokhimiya*, 1968, **10**, 86.
340. R. L. Rebertus, *Anal. Chem.*, 1966, **38**, 1089.
341. I. S. Kirin, Yu. K. Gusev, A. N. Mosevich, N. P. Kuznecov and V. S. Gusel'nikov, *Radiokhimiya* 1965, **7**, 736.
342. C. B. Berger, *Rev. Energ. Primaire*, 1966, **2**, 5.
343. C. B. Berger and M. P. Strier, *NASA Accession No.* N66-15227, Rept. No. NASA-CR-54784 (1965).
344. C. B. Berger, *U.S. Patent* 3,346,422 (1967).
345. F. C. Arrance and D. G. Soltis, *U.S. Patent* 3,421,948 (1969).
346. J. I. Bregman and R. S. Braman, *J. Colloid Sci.*, 1965, **20**, 913.
347. *British Patent* 1,142,586 (1969).
348. E. A. Materova and P. A. Skabichevskii, *Ionnyi Obmen*, *Leningr. Gos. Univ.* 1965, p. 56.
349. K. S. Rajan, J. A. Hunter, W. S. Gillam and H. E. Podall, *U.S. Office Saline Water Res. Develop. Progr. Rept.* 1966, No. 222.
350. G. Alberti and E. Torracca, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1093.
351. E. S. Boichinova and R. B. Chetverina, *Zh. Prikl. Khim.* (*Leningrad*), 1968, **41**, 2656.
352. S. Z. Haider, A. K. Khan and M. K. Rahman, *J. Natur. Sci. Math.* 1966, **6**, 77.
353. V. A. Perevozova and E. S. Boichinova, *Zh. Prikl. Khim.* (*Leningrad*), 1967, **40**, 2679.
354. *Idem*, *ibid.*, 1968, **41**, 1006.
355. *Idem*, *ibid.*, 1970, **43**, 794.
356. E. S. Boichinova and T. I. Podgorelova, *ibid.*, 1967, **40**, 1833.
357. E. S. Boichinova and D. A. Sokolova, *ibid.*, 1965, **38**, 1732.
358. G. S. Martinchik and G. L. Starobinets, *Issled. Svoistv. Ionoobmen. Materialov*, *Akad. Nauk. SSSR*, *Inst. Fiz. Khim.*, 1964, p. 152.
359. V. F. Tikavyi, V. S. Soldatov, G. L. Starobinets and V. A. Labetskii, *USSR Patent* 167,826 (1965).
360. E. S. Boichinova and E. V. Kharitonova, *Zh. Prikl. Khim.* (*Leningrad*), 1965, **38**, 674.
361. K. H. König and K. Demel, *J. Chromatog.*, 1969, **39**, 101.
362. K. H. König, H. Schäfer, F. Hoyer and G. Rassl, *Radiochim. Acta* 1963, **1**, 213.
363. K. H. König and F. Hoyer, *Atompraxis*, 1965, **11**, 275.
364. A. Clearfield, G. D. Smith and B. Hammond, *J. Inorg. Nucl. Chem.*, 1968, **30**, 277.
365. E. Torracca, U. Constantino and M. A. Massucci, *J. Chromatog.*, 1967, **30**, 584.
366. E. Michel and A. Weiss, *Z. Naturforsch.*, *B*, 1967, **22**, 1100.
367. A. Clearfield and W. L. Duax, *Acta Crystallogr.*, *Sect. B*, 1969, **25**, 2658.
368. Yu. D. Sinochkin and D. A. Perumov, *Soosazhdenie i Adsorbtsiya Radioaktivn. Elementov*, *Akad. Nauk SSSR*, *Otd. Obshch. i Tekhn. Khim.*, 1965, p. 140.
369. R. F. Brigevich and R. A. Kuznetsov, *Vestn. Leningr. Univ.*, *Fiz.*, *Khim.*, 1969, 145.
370. J. R. Feuga and T. Kikindai, *Compt. Rend. Acad. Sci.* (*Paris*), *Ser. C*, 1967, **264**, 8.
371. G. R. Popa, G. H. Baiulescu and S. Moldoveanu, *Rev. Chim.* (*Bucharest*), 1966, **17**, 103.
372. N. E. Denisova, E. S. Boichinova and A. A. Peregodova, *Zh. Prikl. Khim.* (*Leningrad*), 1966, **39**, 1235.
373. S. Ahrland, J. Albertsson, L. Johansson, B. Nihlgård and L. Nilsson, *Acta Chem. Scand.*, 1964, **18**, 707.
374. *Idem*, *ibid.*, 1964, **18**, 1357.
375. N. O. Osipova and E. S. Boichinova, *Zh. Prikl. Khim.* (*Leningrad*), 1968, **41**, 2186.
376. K. A. Kraus, *U.S. Patent* 3,382,034 (1968).
377. M. K. Rahman and A. M. S. Huq, *J. Chromatog.*, 1970, **53**, 613.
378. L. Zsinka and L. Szirtes, *Proc. Second Hungarian Conf. Ion-Exchange*, *Balatonszeplak*, 1969, **2**, 627.
379. L. O. Medeiros, *J. Inorg. Nucl. Chem.*, 1966, **28**, 599.
380. T. P. Tang, P. Sun and K.-Y. Chan, *Hua Hsueh*, 1965, 33.
381. T. P. Tam, P. Sun and K.-Y. Chan, *ibid*, 1967, 9.
382. G. Alberti and U. Constantino, *J. Chromatog.*, 1970, **50**, 482.
383. G. Alberti and M. A. Massucci, *German Patent* 1,942,146 (1970).
384. *Idem*, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1719.
385. M. Qureshi and W. Husain, *J. Chem. Soc. A*, 1970, 1204.
386. J. Piret, J. Henry, G. Balon and C. Beaudet, *Bull. Soc. Chim. France*, 1965, 3590.
387. R. Dolique and F. Quenoun, *Trav. Soc. Pharm. Montpellier*, 1966, **26**, 353.

388. *Neth. Appl.* 6,603,607 (1966).
389. *Belg. Patent* 649,389 (1964).
390. G. Alberti, P. Cardini-Galli, U. Constantino and E. Torracca, *J. Inorg. Nucl. Chem.*, 1967, **29**, 571.
391. D. I. Kurbatov and S. A. Pavlova, *Tr. Inst. Khim., Akad Nauk SSSR, Ural. Filial*, 1966, No. **10**, 73.
392. I. K. Tsitovich and M. K. Torpudzhiyan, *Zh. Prikl. Khim. (Leningrad)*, 1967, **40**, 1997.
393. *Idem*, *Sin. Svoistva Ionoobmena Mater.*, 1968, 266.
394. D. Dubos and T. Kikindai, *Compt. Rend. Acad. Sci. (Paris) Ser. C*, 1970, **270**, 1833.
395. G. Balon, C. Beaudet, J. Piret and W. R. Ruston, *Kerntech., Isotopentech.-Chem. Z. Ing. Aller. Fachrichtungen*, 1967, **9**, 258.
396. C. Beaudet, J. Cremer and G. Demaere, *Atompraxis*, 1969, **15**, 165.
397. D. Huys and L. H. Baetslé, *Centre Energ. Nucl. (Brussels)* BLG-422 (1967).
398. G. Alberti, G. Giammari and G. Grassini-Strazza, *J. Chromatog.*, 1967, **28**, 118.
399. M. Qureshi and S. A. Nabi, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2059.
400. G. Alberti and E. Torracca, *ibid.*, 1968, **30**, 3075.
401. M. Qureshi and V. Kumar, *J. Chem. Soc. A*, 1970, 1488.
402. M. Qureshi and H. S. Rathore, *ibid.*, 1969, 2515.
403. C. Cziboly, L. Zsinka and L. Szirtes, *Magy. Kem. Lapja*, 1969, **24**, 470.
404. M. Qureshi and J. P. Gupta, *J. Chem. Soc. A*, 1969, 1755.
405. *Idem*, *ibid.*, 1970, 2620.
406. M. Qureshi and W. Husain, *Separation Sci.*, 1969, **4**, 197.
407. K. H. König and E. Meyn, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1153.
408. K. H. König, E. Meyn and G. Eckstein, *Anal. Chim. Acta*, 1968, **42**, 540.
409. E. M. Larsen and W. A. Cilley, *J. Inorg. Nucl. Chem.*, 1968, **30**, 287.
410. N. Tomota and F. Ichiro, *Asahi Garasu Kogyo Gijutsu Shorei-Kai Kenkyu Hokoku*, 1968, **14**, 563.
411. N. Tomota, F. Ichiro and F. Hisanobu, *Kyoto Daigaku Kogaku Kenkyusho Iho*, 1969, **35**, 22.
412. K. H. König and E. Meyn, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1519.
413. G. Alberti, U. Constantino, P. G. Gregorio and E. Torracca, *ibid.*,1968, **30**, 295.
414. *French Patent* 1,564,350 (1969).
415. K. H. König and G. Eckstein, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1179.
416. G. G. Rocco, J. R. Weiner and J. P. Cali, *U.S. Dept. Com., Office Tech. Serv.* AD 611024 (1964).
417. G. G. Rocco, *ibid.*, AD 610108 (1964).
418. G. Alberti, M. A. Massucci and E. Torracca, *J. Chromatog.*, 1967, **30**, 579.
419. *French Patent* 1,564,349 (1969)
420. G. Alberti, U. Constantino, F. Di Gregorio and E. Torracca, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3195.
421. Y. Inoue, *Bull. Chem. Soc. Japan* 1963, **36**, 1316.
422. *Idem*, *J. Inorg. Nucl. Chem.*, 1964, **26**, 2241.
423. A. Sato, Y. Inoue and S. Suzuki, *Bull. Chem. Soc. Japan*, 1966, **39**, 716.
424. *Idem*, *Sci. Rep. Res. Inst., Tohoku Univ. Ser. A, Suppl.* 1966, **18**, 271.
425. U. Constantino and A. Gasperoni, *J. Chromatog.*, 1970, **51**, 289.
426. Y. Inoue, S. Suzuki and H. Goto, *Bull. Chem. Soc. Japan*, 1964, **37**, 1547.
427. P. De Bruyne, *J. Inorg. Nucl. Chem.* 1970, **32**, 346.
428. Y. Inoue, *Bull. Chem. Soc. Japan*, 1963, **36**, 1325.
429. Pe-Hai Yin and Yung-Hsiang Chu, *Hua Hsueh Hsueh Pao*, 1966, **32**, 103.
430. *Idem*, *K'o Hsueh T'ung Pao*, 1965, 350.
431. M. Qureshi, I. Akhtar and K. N. Mathur, *Anal. Chem.*, 1967, **39**, 1766.
432. M. Qureshi and A. H. Israili, *Anal. Chim. Acta*, 1968, **41**, 523.
433. M. Qureshi, R. Kumar and H. S. Rathore, *J. Chem. Soc. A*, 1970, 272.
434. M. Qureshi, H. S. Rathore and R. Kumar, *ibid.*, 1970, 1986.
435. M. Abe, T. Kenjo and T. Ito, *Kogyo Kagaku Zasshi*, 1967, **70**, 291.
436. M. Abe and T. Ito, *ibid.*, 1967, **70**, 440.
437. M. Qureshi and J. P. Rawat, *J. Inorg. Nucl. Chem.*, 1968, **30**, 305.
438. M. Qureshi and K. G. Varshney, *ibid.*, 1968, **30**, 3081.
439. M. Qureshi, K. N. Mathur and A. H. Israili, *Talanta*, 1969, **16**, 503.
440. L. Zsinka, L. Szirtes and V. Stenger, *Radiochem. Radioanal. Lett.* 1970, **4**, 257.
441. L. Szirtes and L. Zsinka, *Chem. Zvesti*, 1967, **21**, 620.
442. B. Z. Iofa, L. Szirtes and L. Zsinka, *Radiokhimiya*, 1968, **10**, 491.
443. L. Zsinka and L. Szirtes, *Radiochem. Radioanal. Lett.* 1969, **2**, 257.
444. D. Betteridge and G. N. Stradling, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2652.

445. *Idem*, *British Patent* 1,203,581 (1970).
446. *Idem*, *J. Inorg. Nucl. Chem.* 1969, **31**, 1507.
447. P. Remy and A. Boulle, *Bull. Soc. Chim. France*, 1968, 1838.
448. J. Fraissard, P. Remy and A. Boulle, *Compt. Rend. Acad. Sci. (Paris) Ser. B*, 1969, **269**, 66.
449. E. Kobayashi and T. Goto, *Kogyo Kagaku Zasshi*, 1970, **73**, 692.
450. S. D. Grekov and V. A. Leitsin, *Zh. Neorgan. Khim.*, 1968, **13**, 1133.
451. J. A. Bittles, *U.S. Patent* 3,499,537 (1970).
452. V. Pekárek and M. Benešová, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1743.
453. V. Pekárek, V. Veselý and J. Ullrich, *Bull. Soc. Chim. France*, 1968, 1844.
454. V. Veselý, V. Pekárek and M. Abbrent, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1159.
455. V. Pekárek and V. Veselý, *ibid.*, 1965, **27**, 1151.
456. V. Veselý and V. Pekárek, *ibid.*, 1965, **27**, 1419.
457. *Idem*, *Sb. Ref. Celostat. Radiochem. Konf., 3rd, Liblice, Czechoslovakia*, 1964, p. 119.
458. I. G. Lakomkin and N. V. Alekseevskaya, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1965, **1**, 1382.
459. K. Imai, K. Watari and M. Izawa, *J. Nucl. Sci. Technol. (Tokyo)*, 1968, **5**, 485.
460. Yu. V. Morachevskii and V. N. Zaitsev, *Tr. Komis. po Analit. Khim., Akad. Nauk SSSR, Inst. Geokhim. i Analit. Khim.*, 1965, **15**, 260.
461. M. L. Salutsky and M. G. Dunseth, *U.S. Patent* 3,155,454 (1964).
462. M. V. Goloshchapov, S. D. Zhidkikh and T. N. Filatova, *Izv. Voronezh. Gos. Pedagog. Inst.*, 1966, **55**, 8.
463. M. V. Goloshchapov and S. K. Khodzhibaev, *ibid.*, 1966, **55**, 5.
464. *Neth. Appl.* 6,601,903 (1966).
465. V. A. Perevozova and E. S. Boichinova, *Zh. Prikl. Khim. (Leningrad)*, 1968, **41**, 2472.
466. I. K. Vinter, E. S. Boichinova and N. E. Denisova, *ibid.*, 1970, **43**, 1678.

Talanta, 1972, Vol. 19, pp. 263 to 268. Pergamon Press. Printed in Northern Ireland

LE MICRODOSAGE COLORIMETRIQUE DES PHOSPHATES DANS DES MILIEUX DIVERS (PRODUITS BIOLOGIQUES, PHARMACEUTIQUES ET ALIMENTAIRES)

GH. GHIMICESUC et VASILE DORNEANU
Institut de Médecine et de Pharmacie de Iassy, Roumanie

(*Reçu le 7 juillet* 1971. *Accepté le* 2 *octobre* 1971)

Résumé—On propose une microméthode colorimétrique pour le dosage des phosphates dans divers milieux (produits biologiques, pharmaceutiques et alimentaires). Elle est fondée sur leur précipitation à l'état de phosphate double d'uranyle et de magnésium. Le précipité est dissous dans l'acide sulfurique dilué, et l'on dose l'ion uranyle par formation d'une coloration rouge foncé avec le ferrocyanure de potassium, puis mesure au spectrophotomètre. La sensibilité de la méthode est de 0,01 mg de P dans la prise d'essai, l'erreur moyenne est de ±1%. La méthode proposée est très simple et peut être appliquée dans les domaines les plus divers.

DANS LEUR majorité, les techniques couramment utilisées pour le dosage de l'ion phosphate sont fondées sur la formation d'acide phosphomolybdique, ensuite réduit en bleu de molybdène. Ces méthodes diffèrent entre elles par la nature du réducteur utilisé: hydroquinone,[1] acide aminonaphtolsulfonique en milieu sulfitique,[2-4] sulfate d'hydrazine,[5] chlorure stanneux,[6-8] hydroxyquinoléine,[9] *etc.*

Les colorimétries de l'acide phosphomolybdique[10] ou du complexe phosphovanadomolybdique,[11] tous deux colorés en jaune, ont été préconisées ainsi que celle mettant à profit la réaction entre le phosphate d'uranyle et le ferrocyanure de potassium.[12]

D'autres méthodes utilisent le titrage des phosphates par l'acétate d'uranyle en présence de ferrocyanure comme indicateur.

En vue d'établir un procédé unique, applicable à tous les cas considérés, nous avons d'abord étudié la méthode classique avec formation d'un bleu de molybdène. Nous avons constaté que la coloration bleue obtenue est instable, qu'elle s'intensifie dans le temps, et que les résultats ne sont pas reproductibles. Même dans l'intervalle de temps indiqué dans les diverses techniques, la variation d'intensité est appréciable, entraînant des erreurs qui peuvent atteindre 33%.

Notre étude s'est alors orientée vers la colorimétrie du ferrocyanure d'uranyle.[12]

En examinant la précipitation des phosphates à l'état de phosphate d'uranyle, nous avons constaté que la réaction est plus sensible avec l'acétate double d'uranyle et de magnésium (0,01 mg P) qu'avec l'acétate d'uranyle simple (0,1 mg P). Il y a formation de phosphate double d'uranyle et de magnésium, et la réaction n'est gênée par aucun ion.

L'analyse chimique de ce phosphate double, isolé et séché à température ambiante, a conduit à lui attribuer la formule suivante: $Mg(UO_2)_2(PO_4)_2$, 8,5 H_2O. L'analyse thermogravimétrique met en évidence une perte partielle de l'eau de cristallisation vers 105°, et une déshydratation totale vers 200°. Le composé est stable jusqu'à 620°.

Nos essais ont permis l'élaboration d'une technique de dosage des phosphates applicable dans tous les cas considérés (produits biologiques, pharmaceutiques, alimentaires, eaux).

Le principe de la méthode est le suivant: on précipite l'ion PO_4^{3-} sous forme de phosphate double d'uranyle et de magnésium.

$$2\ Na_3PO_4 + 2\ Mg(UO_2)(CH_3CO_2)_4 = Mg(UO_2)_2(PO_4)_2 + 6\ NaCH_3CO_2 + Mg(CH_3CO_2)_2$$

Le précipité est solubilisé dans l'acide sulfurique, libérant les ions UO_2^{2+} d'après la réaction:

$$Mg(UO_2)_2(PO_4)_2 + 3\ H_2SO_4 = 2(UO_2)SO_4 + MgSO_4 + 2\ H_3PO_4$$

Ces ions réagissent alors avec $K_4Fe(CN)_6$, formant $(UO_2)Fe(CN)_6$, sous forme d'une suspension colloïdale rouge foncé qui est mesurée spectrophotométriquement:

$$2(UO_2)SO_4 + K_4[Fe(CN)_6] = (UO_2)_2[Fe(CN)_6] + 2\ K_2SO_4$$

PARTIE EXPERIMENTALE

Réactifs

Etalon de phosphate monopotassique. On dissout 0,1098 g de KH_2PO_4 (désséché pendant 24 h sur acide sulfurique) dans l'eau distillée, q.s.p. 250 ml; 1 ml de cette solution contient 0,1 mg de P ou 0,25 mg de P_2O_5.

Réactif uranyle-magnésium. Solution *a*: on dissout, en chauffant au bain-marie, 10 g d'acétate d'uranyle dans 50 ml d'eau distillée, et ajoute 2 ml d'acide acétique cristallisable. Solution *b*: on dissout, en chauffant au bain-marie, 30 g d'acétate de magnésium dans 50 ml d'eau distillée, et ajoute 1 ml d'acide acétique cristallisable. On mélange à chaud les solutions *a* et *b*, refroidit à température ambiante, et ajoute 400 ml d'alcool 96%. On abandonne pendant quelques heures, filtre, et conserve dans des flacons teintés. La récupération des résidus d'acétate d'uranyl est effectuée selon les indications de E. Kahane (cité d'après la Réf. 13).

Solutions à 10% et 1% d'acide acétique.
Solution à 10% d'acide sulfurique.
Solution à 20% de ferrocyanure de potassium.
Solution à 10% d'acétate de potassium.
Solution à 20% d'acide trichloracétique.
Solution à 5% de soude.
Solution à 5% de persulfate de potassium.

Etablissement de la courbe d'étalonnage

Dans des tubes à centrifuger, on introduit 0,25; 0,5; 1,0; 2,0; 3,0; ... ml de solution étalon de phosphate. On ajoute 1 ml d'acide acétique à 1% et 3 ml de réactif uranyle-magnésium. On agite, puis lave l'agitateur avec 2 ml de réactif. On laisse reposer pendant 30 mn, puis centrifuge. On décante la liqueur claire surnageante, lave le précipité par 3 ml d'eau distillée et répète l'opération jusqu'à ce que la dernière eau de lavage ne donne plus la coloration rouge-brun avec le ferrocyanure de potassium. Après la dernière décantation, on reprend par 1 ml d'acide sulfurique à 10% et agite jusqu'à dissolution complète du précipité. On transvase, en rinçant avec 10–15 ml d'eau distillée, dans une fiole jaugée de 20 ml. On ajoute 2,0 ml de solution à 20% de ferrocyanure de potassium, complète au trait par l'eau distillée, agite, laisse reposer pendant 15 minutes et effectue la lecture à $\lambda = 479$ nm. Les courbes γ-sont des droites passant par l'origine et suivant la loi de Lambert-Beer.

Dosage du phosphore total dans le sang et l'urine

Dans une petite capsule en platine, on introduit 2 ml d'urine diluée au dixième, ou 1 ml de sang ou de sérum, ajoute 1 ml de KOH à 5%, 2 ml de $(NH_4)_2S_2O_8$ à 5% et calcine pendant 1 h dans un four électrique à 700–800. On transfère les cendres obtenues dans un tube à centrifuger avec 1 ml d'acide acétique à 10% et 4 ml d'eau distillée, ajoute 3 ml de réactif uranyle-magnésium et procède ensuite comme déja décrit.

Dosage du phosphore minéral dans le sang (sérum) ou l'urine

Dans un tube à centrifuger de 5 ml, on introduit 1 ml de sang ou de sérum, ou 2 ml d'urine diluée au dixième, ajoute 3 ml d'acide trichloracétique à 20%, agite et centrifuge. La liqueur claire est transvasée dans un autre tube à centrifuger. On lave le précipité à trois reprises avec chaque fois 1 ml d'eau, et les liqueurs surnageantes sont également transvasées dans le tube à centrifuger précédent. On ajoute alors 1 ml d'acétate de potassium à 10%, 5 ml de réactif uranyle-magnésium, et procède ensuite comme déja décrit.

Dosage du phosphore acido-soluble total du sang

A 1 ml de sang, on ajoute 3 ml d'acide trichloracétique à 20% pour éliminer les substances protéiques. On agite et filtre à travers un petit filtre dans une capsule en platine. On lave le précipité à trois reprises avec chaque fois 2 ml d'eau distillée et verse les eaux de lavage dans la capsule. On procède ensuite comme décrit pour phosphore minéral.

Dosage du phosphore lipidique du sang

On verse goutte à goutte 1 ml de sang dans un mélange 3:1 d'alcool éthylique et d'éther sulfurique, agite et filtre à travers un petit filtre dans une capsule en platine. On lave le filtre à trois reprises avec 5 ml du mélange alcool–éther, en recueillant le liquide de lavage dans la capsule. On ajoute 1 ml de KOH à 5%, évapore à sec et calcine dans un four électrique à 700–800. On procède ensuite comme décrit pour phosphore minéral.

La méthode proposée a été vérifiée sur le sang et l'urine, avec ou sans addition d'étalon de phosphate. Les résultats obtenus avec le spectrophotomètre sont consignés dans les Tableaux I–V et montrent que l'erreur relative varie de 0,0 à 2,6%.

TABLEAU I.—PHOSPHORE TOTAL DU SANG

P ajouté, *mg*	P trouvé, *mg*	Différence	Erreur %	Observation
0,00	0,160	0,160	0,0	sang
0,10	0,261	0,161	+0,6	
0,20	0,362	0,162	+1,2	
0,00	0,180	0,180	0,0	sang
0,20	0,379	0,179	−0,6	
0,30	0,479	0,179	−0,6	
0,00	0,148	0,148	0,0	sang
0,10	0,249	0,149	+0,6	
0,20	0,346	0,146	−1,2	
0,30	0,449	0,149	+0,6	
0,00	0,090	0,090	0,0	sérum
0,10	0,189	0,089	−1,0	
0,30	0,390	0,090	0,0	
0,00	0,118	0,118	0,0	sérum
0,20	0,320	0,120	+1,5	
0,00	0,084	0,084	0,0	sérum
0,20	0,284	0,084	0,0	
0,40	0,486	0,086	+0,5	

Dosage du phosphore dans les produits pharmaceutiques contenant du phosphore organique

Dans une capsule en platine, on pèse 0,1 g de produit, ajoute 5 ml de KOH à 5%, évapore à sec au bain-marie et calcine dans un four électrique à 700–800 pendant 1 h. On reprend les cendres par 2 ml d'acide acétique à 10% agite jusqu'à dissolution totale. On transvase quantitativement, au moyen d'eau distillée, dans une fiole jaugée de 100 ml et complète au trait par l'eau distillée.

On introduit 2 ml de cette solution dans un tube à centrifuger, ajoute 3 ml de réactif uranyle-magnésium, et procède comme déja décrit.

La méthode a été vérifiée sur le glycérophosphate de calcium; on a trouvé 14,55% de P au lieu de 14,70 en théorie, soit une erreur de ±1%.

TABLEAU II.—PHOSPHORE MINÉRAL DU SANG

P ajouté, *mg*	P trouvé, *mg*	Différence	Erreur %
—	0,068	—	—
0,20	0,268	0,068	0,0
0,30	0,370	0,070	+3,0%
—	0,084	—	—
0,20	0,284	0,084	0,0
0,30	0,382	0,082	−2,4%
—	0,098	—	—
0,20	0,298	0,098	0,0
0,30	0,396	0,096	−2,0%
—	0,084	—	—
0,10	0,185	0,085	+1,2%
0,20	0,284	0,084	0,0
0,30	0,385	0,085	+1,2%

TABLEAU III.—PHOSPHORE LIPIDIQUE DU SANG

P ajouté, *mg*	P trouvé, *mg*	Différence	Erreur %
—	0,080	—	—
0,10	0,180	0,080	0,0
0,20	0,280	0,080	0,0
0,30	0,382	0,082	+2,6%
—	0,110	—	—
0,10	0,210	0,100	0,0
0,20	0,312	0,112	+1,8%
0,30	0,408	0,108	−1,8%
—	0,082	—	—
0,20	0,281	0,081	−1,2%
—	0,122	—	—
0,20	0,321	0,121	−0,7%
0,30	0,424	0,124	+1,4%
—	0,130	—	—
0,20	0,332	0,132	+1,5%
0,30	0,432	0,132	+1,5%
0,40	0,528	0,128	−1,5%

Produits contenant du phosphore minéral

On pèse 0,1 g de produit, qu'on transfère dans une fiole jaugée au moyen d'eau distillée, complète au trait par l'eau distillée et agite. On introduit 2 ml de cette solution dans un tube à centrifuger, ajoute 3 ml de réactif uranyle-magnésium, et procède comme décrit audessus.

Dosage des phosphates dans les produits alimentaires

On utilise la même méthode. Dans une capsule en platine, on introduit 2 g du produit, on ajoute si nécessaire 2–3 ml d'eau distillée, puis 2 ml de KOH à 5%; on évapore à sec au bain-marie, et calcine dans un four électrique à 700–800. On reprend les cendres par 1 ml d'acide acétique à 10%, transvase quantitativement, au moyen d'eau distillée, dans une fiole jaugée de 50 ml, complète au

TABLEAU IV.—PHOSPHORE TOTAL DE L'URINE

P ajouté, *mg*	P trouvé, *mg*	Différence	Erreur %
—	0,130	—	—
0,20	0,332	0,132	−1,5%
—	0,128	—	—
0,20	0,330	0,130	+1,5%
—	0,110	—	—
0,40	0,510	0,110	0,0
—	0,118	—	—
0,20	0,320	0,120	+1,6%
0,30	0,420	0,120	+1,6%
—	0,125	—	—
0,10	0,224	0,124	−0,8
0,20	0,324	0,124	−0,8
0,30	0,426	0,126	+0,8
—	0,120	—	—
0,20	0,322	0,122	+1,6%
0,30	0,422	0,122	+1,6%
—	0,106	—	—
0,10	0,206	0,106	0,0
0,20	0,308	0,108	+1,9
—	0,064	—	—
0,10	0,163	0,063	−1,3%
0,20	0,264	0,064	0,0

TABLEAU V.—PHOSPHORE MINÉRAL DE L'URINE

P ajouté *mg*	P trouvé *mg*	Différence	Erreur %
—	0,106	—	—
0,30	0,408	0,108	+1,8%
—	0,126	—	—
0,20	0,324	0,124	−1,5%
0,10	0,226	0,126	0,0
0,20	0,325	0,125	−0,7%
—	0,098	—	—
0,10	0,198	0,098	0,0
0,20	0,300	0,100	+2,0%
0,30	0,396	0,096	−2,0%

trait par l'eau distillée, et agite. On introduit 2 ml de cette solution dans un tube à centrifuger, ajoute 3 ml de réactif uranyle-magnésium, et procède comme déja décrit.

La méthode a été vérifiée sur la farine de blé, avec ou sans addition d'étalon de phosphate. Les résultats sont consignés dans le Tableau VI.

CONCLUSIONS

Après étude des méthodes de dosage des phosphates dans les produits biologiques, pharmaceutiques et alimentaires, une mise au point, en tant que technique unique, a été faite de la méthode au phosphate double d'uranyle et de magnésium. Elle comporte la précipitation du phosphate au moyen de l'acétate double d'uranyle et de magnésium, la dissolution du précipité par l'acide sulfurique dilué et le dosage spectrophotométrique de l'ion uranyl après action du ferrocyanure de potassium.

La sensibilité est de 0,01 mg de P dans la prise d'essai, l'erreur moyenne est de ±1 %. La méthode proposée est très simple et peut être aisément appliquée dans les domaines les plus divers.

TABLEAU VI.—PHOSPHORE EN FARINE DE BLE

P ajouté *mg*	P trouvé *mg*	Différence	Erreur %
0,00	0,180	—	—
0,20	0,380	0,181	+0,8
0,10	0,280	0,180	0,0
0,20	0,380	0,180	0,0

Summary—A colorimetric micromethod is proposed for determination of phosphates in various materials (biological substances, pharmaceuticals and food). It is based on precipitation of magnesium uranyl phosphate, which is then dissolved in dilute sulphuric acid, and the uranyl ion is determined spectrophotometrically *via* the dark red colour of uranyl ferrocyanide. The sensitivity is 0·01 mg of P, and the average error 1 %. The method is very simple and applicable to many types of sample.

Zusammenfassung—Es wird eine kolorimetrische Mikrometode für die Dosierung der Phosphaten aus verschiedenen Umfängen (biologische, farmazeutische und Nahrungserzengnisse) vor geschlagen. Sie begründet sich auf das Niederchlagen unter doppelter Farm des Magnesiumsphosphates und uranyl. Der Niederschlag wird in verdünnter Schwefelsäure gelöst unddas uranyl ion wird dosiert durch die Bildung einer dunkelroten Färbung mit K_4 $Fe(CN)_6$ dem welche beim spektrophotometer gemessen wird. Die Empfindlichkeit der Metode ist 0,01 mg P mit einem durchschwittlichen. Fehler von ±1 %. Die vorgeschlagene Metode ist sehr einfach und kann in verschiedenen Umfängen angewendet werdew.

BIBLIOGRAPHIE

1. C. H. Fiske et Y. Subbarow, *ibid.*, 1925, **66**, 375.
2. I. Karpaczy, *Fette Seifen. Anstrichmittel*, 1964, **61**, 748.
3. R. Berg, R. Wölker et E. Skopp, *Mikrochem. (Emich Festschr.)*, 1930, 18.
4. G. Charlot, *Les Méthodes de la Chimie Analytique*, p. 853, Masson, Paris, 1966.
5. D. F. Boltz et M. G. Mellon, *Anal. Chem.*, 1948, **20**, 749.
6. B. Soyenkoff, *J. Biol. Chem.*, 1947, **168**, 447.
7. Gh. Ghimicescu et A. Gheorghiu, *Revue Med. Chir. Soc. Med. Natural. Iasi*, 1947, **58**.
8. Gh. Ghimicescu, C. Ghimicescu et E. Dumbravâ, *Stud. Univ. Babes-Bolyai, Ser. 1*, 1963, 232.
9. R. D. Bell et E. H. Doisy, *J. Biol. Chem.*, 1920, **44**, 55.
10. H. G. Krainick, *Klin. Wochschr.*, 1938, **17**, 706.
11. E. J. King et I. Woolton, *Microanalysis in Medical Biochemistry*, p. 72, Churchill, London, 1959.
12. K. Kroff, *Kinderheilkl.*, 1940, **61**, 601.
13. L. A. Rutkovskii, *Lab. Prakt. (URSS)*, 1940, **15**, 5, 18.

Talanta, 1972, Vol. 19, pp. 269 to 284. Pergamon Press. Printed in Northern Ireland

THE TIN-COLLECTION SCHEME FOR THE DETERMINATION OF PLATINUM-GROUP METALS, GOLD AND SILVER

G. H. FAYE and P. E. MOLOUGHNEY
Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada

(*Received* 30 *March* 1971. *Accepted* 2 *October* 1971)

Summary—A comprehensive analytical scheme is presented for the determination of the six platinum-group metals, gold and silver. It is the result of the integration of separate procedures that have been described previously, in part, over the course of several years. The analytical scheme has been thoroughly tested in umpire and standards work on a wide variety of materials and, as a consequence, is of increasing interest to many laboratories. The precious metals are collected in molten tin when the sample is fused at 1200–1250° with a flux containing stannic oxide, sodium carbonate, silica, borax and flour. The resultant tin alloy is dissolved and the precious metals are isolated by ion-exchange, solvent extraction and/or distillation procedures. With the exception of the usual facilities required in the fusion step of fire assaying, standard equipment can be used in the wet-chemical operations for the isolation and determination of the individual precious metals.

THE LITERATURE reveals numerous problems associated with the determination of gold and silver and the individual members of the platinum-group of metals in ores, rocks, and mineralogical and metallurgical concentrates. Many of the difficulties arise from the use of the time-honoured method of fire assaying in which molten lead is used to collect the precious metals from the fused sample material. The classical lead-collection method is satisfactory for the determination of gold and silver in most commonly encountered materials of mineralogical origin, but there are many instances where it is unsuitable for the determination of the platinum-group metals, and for gold and silver in complex platiniferous materials. The interested reader may refer to certain works by Beamish and co-workers[1–8] for an understanding of many of the problems in the classical method of fire assaying.

To overcome some of these difficulties, certain of the larger mining and metallurgical laboratories employ spectrographic techniques to analyse precious-metal beads produced by the classical method of fire assaying. Although reliable results can be obtained for platinum, palladium, rhodium, and gold, this approach has been unsatisfactory for iridium, ruthenium, and osmium.[8] Further drawbacks to the spectrographic finish, at least for some laboratories, are the cost of equipment and the need for highly trained operators.

Because of the problems indicated above, attempts have been made to develop methods other than those based on the collection of precious metals in lead. Among these are: purely wet-chemical methods, neutron-activation analysis and fire assay methods using a metal other than lead as a collector. Although the first two of these approaches are useful in particular situations, they cannot, as yet, fulfil the need for a versatile method that can be used routinely in a modestly equipped laboratory.

In the early 1960's a new analytical scheme was developed in the Mines Branch for the determination of the platinum metals and gold in ores and other mineralogical materials. This scheme was originally outlined, in part, in 1965 in Research Report R 154 and is based on the preconcentration of the precious metals by a fire assay using tin as the collector.

As at present used, the scheme (Fig. 1) involves the collection of the precious metals in molten tin when the sample is fused at 1200–1250° with a flux containing stannic oxide, sodium carbonate, silica, borax and flour. The resultant tin alloy (containing the precious metals as intermetallic compounds with tin) is then treated by relatively simple wet-chemical techniques to prepare solutions in which the individual precious metals can be determined by methods of atomic-absorption spectrophotometry or classical absorption spectrophotometry. For details of the developmental work involving platinum and palladium,[10] rhodium[11], iridium,[12] ruthenium and osmium,[13] gold,[14] and silver,[15] the reader should refer to the cited papers.

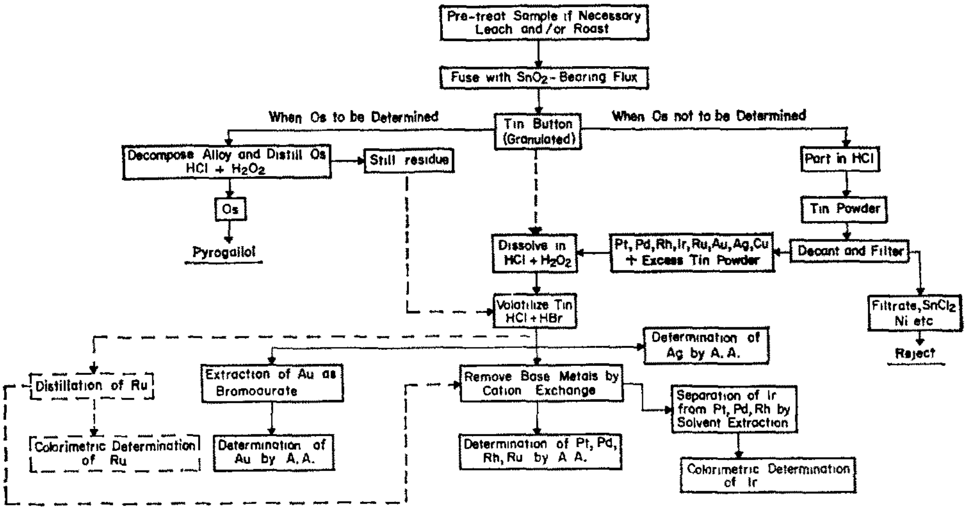


FIG. 1.—Flow-sheet outlining analytical scheme.

The tin-collection scheme has been used routinely in the Mines Branch for about seven years and has been successfully applied to a wide variety of materials including silicate rocks, copper–nickel ores, concentrates and matte, magnetite concentrates, precious metals concentrates, osmiridium and meteorites. In addition to routine applications, the tin-collection scheme of analysis has been used in umpire and standards work where it has been demonstrated, unequivocally, that the results obtained are in good agreement with those obtained by highly developed but less comprehensive methods in other laboratories.

The determination of silver was not part of the scheme described in 1965. Although it was recognized that silver was completely collected in tin, a suitable means was not then available for measuring its concentration in solutions obtained on dissolving the tin button. However, with the combined use of atomic-absorption techniques and tin-collection, silver can now be determined simply and quickly in the most complex materials.[15] Indeed, the silver method seems superior to other methods and, with the exception of materials high in lead, it is highly recommended for most geological and mineralogical samples even if they are not platiniferous.

Atomic-absorption techniques have also been introduced for finishing the determination of gold, platinum, palladium, rhodium and ruthenium; in general this eliminates the need for certain separations necessary before use of colorimetric finishes.

With respect to gold, the combined tin-collection and atomic absorption finish offers the advantages of speed and simplicity over similar procedures using lead as the collector. Again, the former approach is also suitable for many kinds of non-platiniferous materials.

In addition to the inclusion of silver and the introduction of finishes based on atomic-absorption spectrophotometry, a number of other modifications and improvements have been made in the tin-collection method for the precious metals. Because of the continued interest by outside agencies, this paper has been prepared to present the procedural details of the modified and updated tin-collection scheme of analysis for the whole family of precious metals.

GENERAL COMMENTS ON THE ANALYTICAL SCHEME

Certain types of materials such as copper–nickel matte, precious metals concentrates, meteorites and osmiridium may necessitate the determination of all six platinum metals plus gold and silver; Fig. 1 indicates the steps required for these determinations to be made on a single sample. However, many of the operations can be omitted when only partial analysis is required. For example, it is often necessary to determine only platinum and/or palladium because the abundance of these elements in some materials is considerably greater than the abundance of the other precious metals.

There are situations where it may be convenient, and perhaps more rapid, to perform some of the determinations on one portion of sample material (*e.g.*, osmium and/or ruthenium) and proceed simultaneously with the determination of other members of the group on a second portion.

If the sample contains *milligram* amounts of the platinum-group metals, consideration must be given to the recovery and analysis of insoluble residues that may be encountered after the decomposition of the tin button. It is to be emphasized however, that this complication arises only with special materials such as refinery products and bulk samples of native iridium–osmium alloys.

EXPERIMENTAL

Apparatus

The apparatus described below is recommended primarily because it has proved satisfactory in this laboratory; however, it is not necessary to adhere rigidly to the specifications given.

Assay furnace. A 15-kW Globar type with suitable thermocouple and temperature controller. The furnace should be capable of accommodating 6 assay crucibles and maintaining their temperature at 1250°.

Jelrus "Handy-Melt" portable electric furnace. This small vertical furnace is equipped with removable graphite crucibles and is used for melting tin-base assay buttons before their granulation in water. After 4–6 months of relatively constant use, it is recommended that the bottom of the crucibles be examined for small holes.

Atomic-absorption spectrophotometer. It is recommended that this spectrophotometer have a scale expansion facility. An oxidizing air–acetylene flame is used for the determination of gold, silver, platinum, palladium and rhodium; a slightly fuel-rich air–acetylene flame is used for the determination of ruthenium.

Spectrophotometer. The spectrophotometer should be capable of making absorbance measurements in the range 300–800 nm.

Distillation apparatus. The design of the apparatus is shown in Fig. 2. Vessel A is a 500-ml round-bottomed distillation flask and receiver B is a 250-ml, two-necked, round-bottomed flask which, during the ruthenium distillation, is fitted with a 250-ml "Glas-Col" heating mantle. Receivers C and D are 125-ml, tall-form gas-washing bottles with fritted cylinders at the end of the inlet tubes. Each fritted cylinder is pierced to make a 1·5-mm hole to permit free flow of gases through the apparatus.

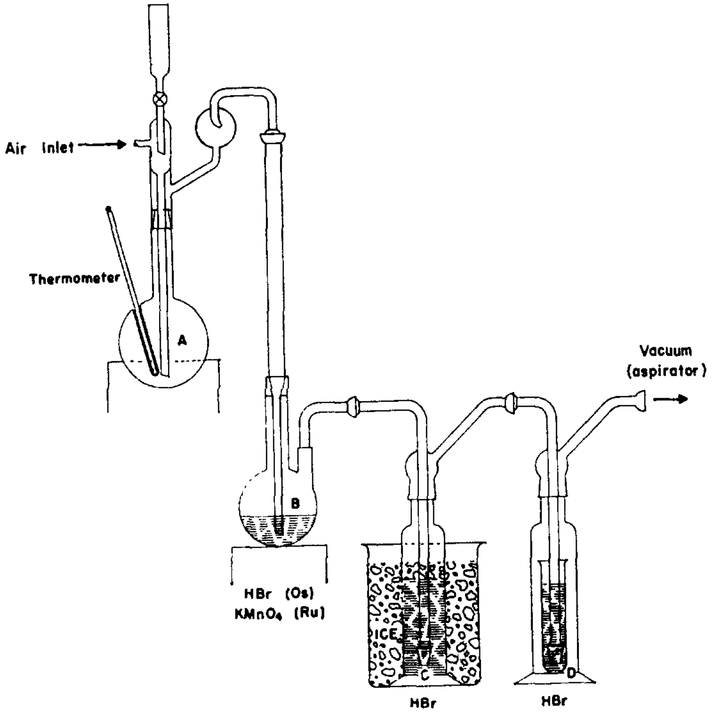


FIG. 2.—Distillation apparatus for osmium and ruthenium. Scale ~ 1/9. Reprinted from *Anal. Chem.*, by permission of the copyright holder (American Chemical Society).

Note. The diameter of the air-cooled, condensing bulb on vessel A should not be less than about 50 mm. A smaller bulb may not be efficient in condensing stannic chloride, which might then be troublesome in the analysis of the distillate.

Cation-exchange columns. It is recommended that both "large" (25 × 450 mm) and "small" (15 × 15 mm) columns be prepared with water-washed, 20–50 mesh, Dowex 50 W-X8 cation-exchange resin. Columns of these dimensions are suitable for the removal of approximately 4 and 0·5 g, respectively, of combined base metals (mainly copper and nickel).

To remove base metals and regenerate the resin, pass 4*M* hydrochloric acid through the column until the effluent solution is free from copper and nickel (test with ammonia solution). Wash the resin with water until the effluent is neutral to litmus paper.

Assay crucibles. Catalogued as "40-gram" type.

Reagents

Details of the preparation of special reagents will be given under *Procedures* in the sections describing their use.

Procedures

A. *Pre-treatment of sample*

Depending upon the nature of the sample, a pretreatment is frequently required to remove certain constituents or convert them into a form that will not lead to difficulties in subsequent operations.

Roasting is used primarily to convert sulphides into oxides, but also to volatilize arsenic and antimony, when present, and thus prevent the formation of matte or speiss during the subsequent fusion. It is recommended that samples other than alloys and copper-nickel matte be roasted before being mixed with the flux. It is known that osmium (but not ruthenium) is lost by volatilization during the roasting operation. Fortunately, this step can be omitted when certain types of platiniferous materials are to be analysed for osmium (*e.g.*, copper-nickel matte).

Place the sample (200-mesh), weighing up to 1 assay ton, in a shallow fire-clay dish and roast at 750–800° for approximately 1 hr with intermittent stirring. In cases where only a few grams of material (particularly sulphides) are to be roasted, place the sample on a thin bed of silica to prevent possible loss of the resultant calcine to the surface of the dish (include the silica used as part of the total quantity required for fluxing–see B1). When the calcine is cool, mix it with the flux and proceed with the fusion process as indicated below in B6.

Leaching of copper-nickel matte can be conveniently achieved in the following manner to remove the bulk of the copper and nickel and to leave the precious metals in a concentrated form in the leach residue. Place the sample, weighing up to 2 assay tons, in a 1500-ml beaker and treat it with approximately 25 g of ammonium chloride and 100–200 ml of 12*M* hydrochloric acid. Heat the covered beaker and contents until the amount of insoluble matter appears not to exceed approximately 2 g. If dealing with large sample weights, it may be necessary to retreat the leach residue once or twice with fresh acid after intervening filtrations.

Dilute the combined sample solution (approximately 100 ml) with an equal volume of water, heat to approximately 70° and then stir the solution and dissolved residue with a polyethylene-coated, electrically-driven stirrer. Add approximately 5 g of tin powder (200-mesh or finer) and stir the suspension for approximately 15 min. Filter the solution, containing most of the nickel, through a moderately fast paper. Completely wash the solids onto the paper with dilute (~5%) hydrochloric acid. Dry the washed residue and paper at ~110° for about 1 hr and then mix them with the flux for fusion (B6). [*Note.* After the fusion of the matte leach residue, a small amount of a sulphide phase will adhere to the tin button but this will ultimately be decomposed during the chemical treatment of the button (C1).]

Acid attack of the metallic phase from meteorites is necessary because the meteoritic iron–nickel alloy would not be attacked appreciably during the fusion process on account of the relatively low temperature and the reducing conditions that prevail. This problem can be avoided by dissolving the alloy in hydrochloric acid and then fusing the resultant chloride salts as in B6 below. The net result is to slag off the iron and collect the precious metals in the tin button.

Dissolve the meteoritic alloy (preferably more than 5 g of granules or turnings) in the requisite amount of boiling 12*M* hydrochloric acid. Evaporate the solution to dryness directly on the hot-plate and near the end of the operation stir the crystallizing salts with a glass stirring rod. The heating should be carried out in such a way as to drive off as much free acid as possible yet keep the mass from baking; this is to lessen the possible danger of losing osmium as the volatile tetroxide.

Scrape the dried salts from the beaker and add to the flux as described in B6(*a*). Using small portions of water and a rubber policeman, dissolve and dislodge the remaining material adhering to the beaker and pour the solution (suspension) into a bed of the standard flux.

B. *Crucible fusion process (preparation of buttons)*

1. *Flux.* The flux that has proven most satisfactory for nearly all materials so far encountered, contains the following materials in the indicated quantities:

	g
SnO_2	35–40
Na_2CO_3	50
SiO_2	10–20
$Na_2B_4O_7$	10
Flour	40

The quantity of silica is adjusted according to the amount of silica in the sample (for details see B4 below).

Note. Powdered coke (100–325 mesh) is also satisfactory as a reducing agent, 6–8 g being required. In early work[9–15] coke was used as reducing agent because experiments had shown that the use of relatively small quantities of flour (~10 g) resulted in the formation of inordinately small buttons. Subsequently however, it was learned that by increasing the amount of flour to 40 g, essentially complete reduction of stannic oxide is achieved. With 120 g of the flux, 40 g of flour, and samples weighing up to 1 assay ton (29·17 g), tin buttons weighing 27–29 g are obtained. This represents 85–90% recovery of the tin.

2. *Amount of sample required for analysis.* Usually the analyst has some prior knowledge of the range of the platinum metal and base metal values to be expected and can make a choice of sample weight according to the following considerations.

With the atomic-absorption methods described later in this paper, the smallest amounts of the individual precious metals that can be determined with reasonable accuracy are, in μg: Pt $\sim$ 5, Pd $\sim$ 1, Rh $\sim$ 1, Ru $\sim$ 5, Au $\sim$ 2, Ag $\sim$ 1. If the colorimetric methods are used for the platinum metals, the corresponding values are $\sim$3 μg each for Pt, Pd, Rh, Ir, Ru and $\sim$10 μg for Os.

To determine smaller quantities of the precious metals than indicated above, replicate buttons from 1-assay-ton samples, for example, can be combined and analysed by the methods to be described.

3. *Behaviour of copper and nickel during fusion.* During the crucible fusion process, virtually all of the nickel and copper in the charge form an alloy with the tin, while the iron remains in the silicate slag. Experience has shown that it is desirable to keep the combined nickel and copper content of the button to less than approximately 4 g.

Copper and, particularly, nickel increase the melting point of the assay button. Therefore, when more than 1–2 g of the base metals is expected to be present, approximately 10 g of tin (stick-tin is a convenient form) can be added to the charge to reduce the melting point of the button and thus facilitate the granulation process [B6(*c*)].

4. *Variation of composition of flux with nature of samples.* In contrast to the classical method of fire assaying, the flux and the proposed fusion process need not be modified greatly when processing materials of a diverse nature. However, minor variations in the charge are made with certain types of materials; these are indicated below together with a general description of the kinds of material to which the proposed analytical scheme may be applied.

Siliceous ores and rocks. For a 1-assay-ton sample of such materials, the quantity of silica used in the flux may be varied from 20 to 10 g, depending on the estimated silica content of the sample. Platiniferous rocks are frequently of the ultrabasic type such as dunite, pyroxenite, *etc*, and these contain the precious metals in minute, widely dispersed blebs of native platinum or perhaps minerals such as iridosmine. Because of the possible heterogeneity of samples of such rocks, reproducible results may not be obtained.

Magnetite and ilmenite. Experiments have shown that essentially complete decomposition is achieved with charges containing as much as 15 g of either of these minerals. The relatively large amount of iron or titanium in these minerals to be reduced to lower states of oxidation requires the use of approximately 40 g of flour in the fusion of a 1-assay-ton sample. Usually platinum is the predominant precious metal in these minerals.

Copper–nickel sulphide ores and concentrates. Because of the relatively large amounts of base metal oxides that may be present (after roasting) and must undergo reduction, 40 g of flour are required in the fusion of a 1-assay-ton sample.

Copper–nickel sulphide ores are among the most commonly encountered naturally platiniferous materials. Although minute grains of platinum metal-bearing minerals, such as sperrylite ($PtAs_2$), michenerite ($PdBi_2$), and froodite ($PdBi_2$) are known to occur in these sulphides, it is considered by some workers that the platinum metals are present, not as discrete compounds or minerals but, rather, in solid solution in the base metal minerals pentlandite, pyrrhotite and chalcopyrite.

All members of the platinum metals group are known to occur in certain copper–nickel sulphide deposits; however, palladium and platinum are the predominant metals. Other members of the group are usually less abundant by a factor of 5–10.

Iiridosmine (*osmiridium*). This native alloy, as the name suggests, is composed mainly of osmium and iridium and occurs in placer deposits in the form of flattened grains. Iridosmine is among the most chemically inert minerals known, but it seems to be completely attacked by molten tin during the crucible fusion process[12,13] of the proposed analytical scheme, the osmium and iridium forming intermetallic compounds with tin (shown by electron microprobe analysis of tin buttons). Thus, the precious metals in minute grains of iridosmine occurring in ores or concentrates would be reported together with the values from other minerals.

It is to be emphasized that the accurate, complete analysis of *bulk* samples of native alloys such as those of the osmium–iridium series would involve specialized methods of decomposition such as dry chlorination, rather than the procedures outlined here.

Chromite. Chromite is not completely decomposed during the fusion process, and samples containing an appreciable proportion of it must be subjected to a pretreatment that will decompose it. This can be done by sintering with sodium peroxide. The sample is mixed with 1·5 times its weight of sodium peroxide; placed on a 10-g bed of silica in a roasting dish and roasted at 700° for about 1 hr. The sinter cake and underlying silica are ground together in a mortar and mixed with the flux for the crucible fusion process. The weights of sodium peroxide and silica are subtracted from the weights of sodium carbonate and silica, respectively, in the flux described in B1.

5. *Gold and silver content of stannic oxides and tin powder.* Experience has shown that both stannic oxide and tin powder invariably contain a significant concentration of both gold and silver (*e.g.*, ~0·1–2·0 ppm). It is therefore imperative that the gold and/or silver value of each batch of these materials be determined and subtracted as a blank when the determination of either of these metals is included in the analytical scheme. Despite the necessity of making corrections for the blank, accurate and reproducible results are easily obtained with the procedures to be described.

6. *Procedures for preparation of buttons.*

(*a*) *Mixing the charge.* For dry samples follow the standard assay practice by blending the dry samples with the flux on glazed paper and transfer the charge to a "40-gram" crucible.

When solutions or suspensions (*e.g.*, from acid decomposition of meteorites) are to be mixed with the flux, place approximately one third of the standard flux in the crucible and press a square of thin, commercial, plastic wrapping-film into the crucible to form an envelope, and into this envelope transfer the remainder of the flux. With a spatula, form a cavity in the bed of flux and transfer the sample slowly into the depression so as to avoid wetting the film or crucible walls. Heat the crucible and contents in a drying oven at 110° for at least 2 hr. After the sample has dried, remove the material in the wrapping-film envelope and grind it in a mortar, mix well, and place back in the film in the crucible.

(*b*) *Fusion.* Place the crucible in an assay furnace maintained at approximately 1250° and fuse the contents for 1 hr. During the first 15 min, inspect the crucible several times to ensure that evolution of gases, or frothing, is not excessive. On the few occasions when this situation arises, swirl the molten material in the crucible several times with tongs until the melt becomes quiescent, then continue the fusion. At the completion of the fusion period, the melt should not be viscous or lumpy nor should there be extensive crust formation at the top of the melt.

Pour the melt into a conical steel mould and, when it is cool, separate the tin button from adhering slag by tapping with a small hammer. (A small file can sometimes be used to advantage in removing tenaciously adhering encrustations of slag, but loss of metal should be avoided.)

(*c*) *Granulation of buttons.* Place the button in the graphite crucible of the Jelrus furnace (see *Apparatus*), from which air is purged by nitrogen gas delivered through a suitable ceramic tube placed directly over the button. After melting the button (which may require a temperature of 600–700° for buttons particularly rich in nickel), withdraw the nitrogen delivery tube and, using tongs to hold the crucible, quickly pour the molten tin-alloy into approximately 1 gallon of water contained in an enamel pail. Decant the water; dry the alloy on the hot-plate (avoid remelting). Any large lumps produced can easily be reduced in size with metal shears.

Reserve the granulated alloy for analysis according to the appropriate procedures described below and outlined in Fig. 1.

C. *Wet chemical procedures for isolation, separation and determination of precious metals*

1. *Decomposition of tin buttons (except when osmium is to be determined).* Two procedures for the decomposition of the tin button may be used, the choice being largely dependent on the nature of the sample.

The procedure used by the authors for most materials involves treatment (parting) of the tin-alloy with concentrated hydrochloric acid. A major proportion of each of the precious metals, as intermetallic compounds of tin, remains undissolved; however, a significant fraction especially of rhodium, iridium and ruthenium, dissolves along with the tin matrix. The soluble species are readily recovered by cementation with tin powder.

The major advantage of the hydrochloric acid parting-procedure is that much of the excess of tin, as stannous chloride, can be eliminated before the tin-volatilization procedure.

If the sample contains *milligram* amounts of the platinum-group metals it is advantageous to decompose the tin-alloy directly with a mixture of hydrochloric acid and hydrogen peroxide. Insoluble matter which may remain is easy to recover and treat chemically. A minor disadvantage of this approach is that subsequently all the tin of the original button may have to be volatilized.

(*a*) *Parting in hydrochloric acid.* Transfer the granulated tin alloy to a 600-ml beaker and treat it with approximately 150 ml of concentrated hydrochloric acid. Cover the beaker with a clock-glass and heat until the alloy has been decomposed and vigorous evolution of bubbles from the black insoluble residue has ceased. Dilute the resulting suspension to about 400 ml with water and heat to approximately 70°. While the suspension is being stirred with a motor-driven polyethylene-coated stirrer or magnetic stirrer, sprinkle approximately 5 g of powdered tin (200-mesh or finer) into the beaker to precipitate any precious metals that had dissolved during the parting operation. Stir the contents of the beaker for approximately 15 min.

If iridium and/or ruthenium are to be determined, again heat the beaker to approximately 70° and add a second 5-g portion of powdered tin; stir for an additional period of 15 min.

If silver only is to be determined, the hydrochloric acid solution need not be heated and not more than 0·5 g of tin powder is required.

The insoluble matter produced in these operations should contain essentially all the copper in the sample, the excess of tin powder, and all of the precious metals. Nickel remains in solution and is ultimately discarded.

Decant the supernatant solution through a pad of paper pulp (from Whatman No. 31 paper) supported on a filter disk. Wash the solids several times by decantation with $1M$ hydrochloric acid and pass the washings through the filter pad.

Add 25–30 ml of $12M$ hydrochloric acid to the solids in the beaker, and then cautiously add 30% hydrogen peroxide in small portions until the solids have dissolved and excess of peroxide is present. A small amount of siliceous matter from the slag may be present, but can be ignored. After the mixture has been heated to the boil for a few minutes to ensure complete dissolution of the residue, place the beaker under the filter pad and wash the pad with a mixture of approximately 10 ml of $12M$ hydrochloric acid and 2–3 ml of 30% hydrogen peroxide to dissolve any fines caught on the filter during decantation.

Analyse the solution obtained in these operations for silver as in C2, or treat directly as in C3 to voltilize tin if silver is not to be determined.

(*b*) *Decomposition in hydrochloric acid and hydrogen peroxide* (primarily for samples containing milligram amounts of the platinum-group metals). Place the granulated tin alloy in an 800-ml beaker immersed in an ice-bath. Add approximately 200 ml of $12M$ hydrochloric acid, then with stirring cautiously add 30% hydrogen peroxide in relatively small portions until the tin alloy has decomposed and the effervescence from excess of peroxide is evident. Add an additional 50 ml of hydrochloric acid and 10 ml of hydrogen peroxide then heat the beaker and contents until the volume of the solution has been reduced to approximately 100–150 ml.

Dilute the solution with approximately 100 ml of water and allow any dense, dark-coloured residue to settle for about 30 min. Decant the supernatant solution through an appropriate filter paper into a 500-ml volumetric flask. Wash the beaker and residue, by decantation, with several small portions of dilute hydrochloric acid.

Treat any residue left in the beaker with approximately 10 ml of $12M$ hydrochloric acid and 5 ml of 30% hydrogen peroxide. Evaporate the solution to a small volume, then add 5–10 ml of *aqua regia*. Again evaporate the solution to 1–2 ml and, by repeated treatments with $12M$ hydrochloric acid, destroy nitrogen-containing compounds and ensure that the platinum metals are present as their chloro-complexes. Dilute the acid solution with a small volume of water then filter into the 500-ml flask through the paper used previously.

Dry the paper and residue and then fuse as in B6, to produce a second tin button. Decompose this, in turn, with hydrochloric acid and hydrogen peroxide. Filter off any siliceous matter from the resulting solution and receive the filtrate in the 500-ml flask containing the solution from the first button. Dilute to volume with water.

Because this method of decomposition is used primarily for materials rich in platinum-group metals, it is often sufficient to take an aliquot of the sample solution for analysis by the procedures described below.

If the solution obtained by C1(*b*) is to be analysed for silver, take an appropriate aliquot and adjust to approximately $2M$ hydrochloric acid before atomization as in C2. When a large aliquot is taken and it must be reduced in volume to concentrate silver, it may be necessary to volatilize tin by procedure C3 before the determination of silver by atomic absorption.

2. *Determination of silver by atomic absorption.*[15] To prevent possible blockage of the atomizer by particulate matter, filter the combined solution obtained by the procedure C1 through a fast paper (*eg*., Whatman No. 31) into a 200-ml volumetric flask. Wash the filter paper several times with water, and dilute the combined filtrate and washing to volume. The resultant solution for atomization should be approximately $2M$ in hydrochloric acid.

If milligram quantities of silver are present, filter this solution into a 500-ml flask and adjust the hydrochloric acid and concentration to approximately $3M$ to prevent precipitation of silver as the chloride.

Take an appropriate aliquot, and adjust to $2M$ hydrochloric acid before atomization. The aliquot may contain up to 4 ppm of silver. Reserve the remainder of the solution from the tin-button decomposition for the determination of the platinum metals and/or gold by the procedures to be described below.

Determine the silver content of the aliquot by atomic absorption, using a wavelength of 328·1 nm, a 0·10-m narrow-slit burner and an oxidizing air–acetylene flame. Subtract the silver content of the blank from that of the sample.

3. *Volatilization of tin before the determination of gold and platinum-group metals.* Evaporate the solution from either C1 or C2, above, to a relatively small volume on the hot-plate, then place the beaker in an aluminium "no-bump" solution evaporator. Heat the evaporator from below with the hot-plate and from above with an infrared heat lamp to volatilize as much tin as possible.

Copious fumes of stannic halide are evolved at this point, and, when relatively large amounts of copper and/or nickel are present, care should be taken to avoid spattering caused by local intense heating.

When it appears that the evolution of fumes has nearly ceased, remove the beaker from the evaporator and cool for a short time. Wash down the sides of the beaker with approximately 10 ml of a mixture (7:2) of hydrochloric and hydrobromic acids and again evaporate to dryness under the heat lamp. Repeat the treatment with the mixed halogen acids (5–10 ml) and the evaporation twice or until it is evident that essentially all of the tin has been volatilized.

If gold is to be determined, simply evaporate the mixed halogen acid solution as in C4 below.

If gold is not to be determined, cool the beaker and residue, add 10–15 ml of $12M$ hydrochloric acid, and then, while swirling the beaker in a fume cupboard, cautiously add 30% hydrogen peroxide until it is evident that an excess of peroxide is present and that the evolution of bromine vapour is not vigorous. Evaporate the solution to small volume and process according to requirements (see flow sheet) for the removal of base metals or the extraction of gold and/or the distillation of ruthenium.

4. *Isolation and determination of gold.* Evaporate the solution to 2–3 ml. If the solution does not contain an appreciable quantity of base-metal chlorides, place the beaker in a hot water-bath and, with the aid of a jet of compressed air, evaporate the solution gently to dryness to prevent baking of the gold salts on the beaker walls. When a substantial amount of base-metal chlorides is present, the solution can be evaporated gently to dryness directly on the cooler part of the hot-plate.

Take up the salts in 5 ml of $2M$ hydrobromic acid and wash into a 60-ml separatory funnel with a further 10 ml of $2M$ hydrobromic acid. Extract the gold by shaking the solution with two separate 15-ml portions of diethyl ether. Double the volume of hydrobromic acid and ether if the sample contains a relatively large quantity of copper. Combine the ether extracts and wash with three separate 5-ml portions of $2M$ hydrobromic acid. Strip the gold from the ether phase by shaking it with three separate 15-ml portions of water. Treat the aqueous gold solution with approximately 2 ml of *aqua regia* and evaporate to a small volume. Transfer the gold solution to a volumetric flask of appropriate size, depending upon the expected gold content, and dilute to volume with water. Determine the gold content of the solution by atomic-absorption as described below.

Evaporate to dryness the aqueous phase from the ether extraction of gold and, with a small volume of hydrochloric acid–30% hydrogen peroxide mixture (2:1), destroy bromides and convert the metals into their chlorocomplexes. Reserve the resulting solution for the determination of platinum-group metals according to the procedures given below.

Determine the gold content of the final solution, containing at least 0·2 ppm of gold, by atomic absorption at a wavelength of 242·8 nm, a 0·10-m narrow-slit burner, and an oxidizing air–acetylene flame. Subtract the gold content of the blank charge from that of the sample.

5. *Some comments on the anaytical scheme for the platinum-group metals.* Most samples to which the proposed methods will be applied will require the determination of one or more of platinum, palladium, and rhodium with or without the prior determination of gold and/or silver. When this is the case, the procedures described immediately below for removing base metals by cation-exchange, followed by the individual determination of platinum palladium, and rhodium by atomic absorption or colorimetric techniques, can be followed directly.

However, as will be seen subsequently, the scheme must be altered somewhat when osmium, and possibly ruthenium, is to be determined on the same assay buttons as the other precious metals. The distillation procedures for isolating osmium and ruthenium (only when ruthenium is to be determined colorimetrically) must be applied before the determination of gold, platinum, palladium, rhodium and iridium. Although this is a perfectly feasible analytical path, it may be more convenient, if sufficient material is available, to determine osmium and ruthenium (colorimetrically) on a separate sample.

It should be noted that the comments above pertain to ruthenium only if this element is to be determined colorimetrically; if atomic-absorption spectrometry is to be used for ruthenium, then this element need not be isolated by distillation and can be determined in the same solution as that containing platinum, palladium and rhodium.

The atomic-absorption sensitivity for iridium is low, therefore the proposed analytical scheme involves the use of the more sensitive colorimetric determination of iridium after it has been separated from other platinum-group metals by solvent extraction. If the iridium content of the sample is relatively high, however, as in precious metal concentrates, then iridium too can be determined by atomic-absorption.

6. *Removal of base metals by cation-exchange*[16,17,18] *before the determination of the platinum-group metals.* Evaporate the solution of metal chlorides to dryness. Take up in 5–10 ml of 12 M hydrochloric acid and again evaporate to a residue of salts. When more than approximately 0·5 g of base metals (usually copper) is present, stir the crystallizing salts with a stirring rod to aid in the removal of free hydrochloric acid. Cool the beaker and, depending on the amount of base metals estimated to be present, add 0·25 or 0·50 ml of $12M$ hydrochloric acid and then dissolve the salts with 50 or 100 ml of water, to give a solution with a pH of 1·0–1·5.

Notes: (1) At this point the analyst should be aware of the possibility of hydrolysis of the anionic chloro-complexes of rhodium, iridium and, especially, ruthenium during the ion-exchange process. In the operating time required, hydrolysis can be prevented by maintaining the chloride ion concentration at 0·1*M* or higher, which is normally provided by the base metal salts present. However, when it is apparent that these are in low concentration, it is advisable to add approximately 0·5 g of sodium chloride per 50 ml of solution.

(2) If the sample solution contains appreciable quantities of base-metal chloro-salts, *i.e.*, a relatively high chloride ion concentration, any silver present may remain in solution until a later stage when the chloride ion concentration has been reduced, for example in 8(*c*).

Pass the sample solution through a cation-exchange column at the rate of approximately 5 ml/min. If the sample contains less than approximately 0·5 g of base metals, use a "small" column; otherwise use a "large" column as described under *Apparatus.* Collect the effluent solution in a 400-ml beaker and wash the column with sufficient dilute hydrochloric acid (pH approx. 1) to quadruple the original volume of the sample solution.

To the effluent solution, add approximately 25 mg of sodium chloride and 10 ml of 12*M* hydrochloric acid and reserve for the separation of platinum, palladium, rhodium and iridium or for the isolation of ruthenium by distillation (see Fig. 1).

Notes: (1) In certain cases it may become apparent, from the colour developed during the subsequent evaporation of the effluent solution, that leakage of base metals has occurred. This can generally be ignored if the solution is to be analysed by atomic absorption for one or more of platinum, palladium and rhodium. However, it is necessary to repeat the cation-exchange operation (using the small column) to remove the contaminants if colorimetric finishes are to be used.

(2) If tin were not completely volatilized in earlier steps, it would precipitate in a gelatinous or flocculent form during the ion-exchange process and might contaminate both the resin bed and the effluent solution. If the amount of precipitate is relatively small (slightly cloudy suspension), then the danger of losing platinum metals by occlusion or co-precipitation is slight and, therefore, any solid material retained on the resin bed can be neglected. The small amount of tin in the effluent can be removed ultimately by repeating the volatilization procedure given above in C3. When more than a few milligrams of tin appear to be present, strip the column with 4*M* hydrochloric acid, combine the stripping solution with the original effluent and treat the whole, as above, for the volatilization of tin before repeating the ion-exchange procedure.

7. *Atomic-absorption determination of platinum, palladium, rhodium and ruthenium.*

Mixed cadmium–copper sulphate. Prepare a solution[19] by dissolving 98·0 g of $CuSO_4 . 5H_2O$ and 57·0 g of $3CdSO_4 . 8H_2O$ in 500 ml of 12*M* hydrochloric acid and 300 ml of water. Dilute to 1 litre with water.

Evaporate the sample solution, containing a mixture of the platinum metals as their chloro-complexes, from C6 above, to incipient dryness in the presence of a few milligrams of sodium chloride. Add 5 ml of the cadmium–copper sulphate solution and dilute to 25 ml with water. Filter the solution if a cloudiness develops.

In certain cases it may be necessary to prepare a more concentrated solution for the determination of the minor elements, followed by dilution of aliquots for the determination of the other metals.

The aliquot taken for analysis should contain at least 1 ppm of each of platinum and ruthenium or 0·2 ppm of each of palladium and rhodium. The wavelengths used for these elements are respectively 266·1, 349·9, 247·8 and 343·6 nm. An oxidizing air–acetylene flame is used for the determination of gold, silver, platinum, palladium and rhodium; a slightly fuel-rich air–acetylene flame is used for the determination of ruthenium.

8. *Separation of platinum, palladium, rhodium and iridium*[20] (before colorimetric determination).

(*a*) *General comments.* Previously it was mentioned that the atomic-absorption sensitivity for iridium is relatively low, therefore it is often necessary to determine this metal colorimetrically. This necessitates the separation of iridium from the other platinum-group metals, each of which interferes with its determination. The following solvent extraction scheme is used for such a separation.

Procedures are also given for the fractionation of mixtures of platinum, palladium and rhodium because they are required if these metals must also be determined colorimetrically rather than by the more convenient atomic-absorption technique. Because the determination and separation of palladium with *p*-nitrosodimethylaniline are so closely related, the procedure for its colorimetric determination is included.

(*b*) *Special reagents. Equilibrated tri-n-butyl phosphate TBP)* prepared by shaking the purified grade of TBP with an equal volume of 6*M* hydrochloric acid in a separatory funnel for approximately 1 min. *Buffer, pH* 2·2, prepare by mixing 50 ml of 4*M* sodium acetate (33 g/100 ml) with 53 ml of 4*M* hydrochloric acid. *Ethanolic* p-*nitrosodimethylaniline solution* 0·5%, prepared by mixing 0·5 g of *p*-nitrosodimethylaniline with 100 ml of 95% ethyl alcohol, leaving over-night (or placing in an ultrasonic bath for a few minutes), and filtering off any solids on Whatman paper No. 30.

(*c*) *Separation of platinum and palladium from rhodium and iridium.* Evaporate the sample solution, containing a mixture of the platinum metals as their chloro-complexes, from C6 above, to incipient dryness in the presence of a few mg of sodium chloride. Dissolve the salts in 8–10 ml of approximately 1*M* hydrochloric acid, and allow to stand for a few minutes to allow any silver that may be present to precipitate as the chloride. If necessary, remove the silver chloride by filtering the solution through a No. 40 paper, directly into a 60-ml sepatatory funnel. Adjust the volume of solution to 20 ml and the hydrochloric acid concentration to 6*M*. Shake the sample solution with 5 ml of an aqueous 4% w/v solution of sodium iodide and allow the mixture to stand for about 30 min. Extract the platinum and palladium iodide complexes with two separate 15-ml portions of a 15% solution of TBP in hexane. Withdraw the aqueous phase, wash it with 10 ml of hexane in a separatory funnel, and then reserve it for the separation of rhodium and iridium as in (*f*) below.

Combine the TBP-hexane extracts and strip the mixture of platinum and palladium by shaking it with three separate 10-ml portions of concentrated nitric acid for approximately 20 sec each. Place the nitric acid stripping solution in a separatory funnel, dilute with an equal volume of water, and shake with 10 ml of hexane to wash out as much TBP as possible.

If the sample solution is expected to contain 50 μg or less of palladium, transfer it to a beaker and treat as in (*d*) and (*e*) for the determination and/or separation of palladium. When the sample solution is expected to contain more than 50 μg of palladium, dilute it to a known volume and remove a suitable aliquot for the separate determination of palladium. In the latter case, place both the aliquot and the remainder of the solution in separate beakers and treat as in the following procedure.

(*d*) *Determination of palladium with* p-*nitrosodimethylaniline.*[21] Treat the platinum–palladium solution obtined in (*c*) with a few mg of sodium chloride and evaporate to incipient dryness. To convert platinum and palladium into their chloro-complexes, add 2–3 ml of 12*M* hydrochloric acid, evaporate the solution just to dryness, then repeat these operations twice ensuring that all excess of acid has been removed by evaporation. Add 2 ml of the sodium acetate-hydrochloric acid buffer solution and approximately 10 ml of water to the residue in the beaker. Warm the mixture gently for a few minutes and, with aid of a rubber policeman, loosen any sticky deposits that may be adhering to the bottom of the beaker.

When palladium is to be determined (in the whole sample solution or an aliquot), add 1 ml of the 0·5% solution of *p*-nitrosodimethylaniline and transfer the red solution to a 50-ml volumetric flask. Wash the original beaker with 15 ml of 95% ethyl alcohol, add the washings to the flask, and dilute to volume with water. Measure the absorbance of the solution at 525 nm, and then determine the palladium content of the sample by reference to a calibration curve prepared from spectrophotometric data obtained from standard solutions that have been taken through the TBP extraction procedure.

(*e*) *Separation of palladium from platinum. Note*: This separation is based on the fact that at room temperature platinum does not react appreciably with *p*-nitrosodimethylaniline[18] and thus it remains in the aqueous phase when the palladium–*p*-nitrosodimethylaniline complex is extracted with chloroform.

Combine the portion of solution taken for spectrophotometric measurement with the remainder of the platinum–palladium solution and transfer the whole to a 60-ml separatory funnel and reserve for the separation of palladium from platinum. When the sample contains 50 μg or more of palladium, add 2 ml of the *p*-nitrosodimethylaniline reagent and 15 ml of ethyl alcohol, and transfer the mixture to a 60-ml separatory funnel.

Extract the palladium–*p*-nitrosodimethylaniline complex with two or three separate 10–15-ml portions of chloroform. If mg amounts of palladium are to be separated, add an additional 1–2 ml of *p*-nitrosodimethylaniline reagent and continue the extraction with further portions of chloroform until the aqueous phase is light yellow or colourless.

Filter the aqueous phase (or an aliquot) through a Whatman No. 31 paper into a 400-ml beaker, add approximately 2 ml of concentrated sulphuric acid and approximately 10 ml of concentrated perchloric acid. Reserve this solution for the spectrophotometric determination of platinum by a suitable colorimetric method.[10,22]

(*f*) *Separation of iridium from rhodium.* Transfer the rhodium–iridium fraction obtained in (*c*) to a 250-ml beaker, evaporate nearly to dryness, and treat with a few drops of concentrated nitric acid to destroy iodides. Convert the rhodium and iridium into chloro-complexes by the repeated addition and evaporation of 2–3-ml portions of 12*M* hydrochloric acid and 1 ml of 30% hydrogen peroxide (to ensure that iridium remains in the quadrivalent state) and wash the resultant solution into a 60-ml separatory funnel with an additional 5 ml of 6*M* hydrochloric acid. Add 5 ml of equilibrated TBP and 5 ml of hexane and shake the funnel and contents for 1 min. Transfer the lower (aqueous) phase to a second funnel and repeat the extraction step. Drain the aqueous phase into a clean separatory funnel, wash with approximately 10 ml of hexane, and reserve for the determination of rhodium by a suitable colorimetric method.[11,23]

Combine the two TBP-hexane extracts in a separatory funnel and strip the mixture by shaking it with three separate 15-ml portions of dilute hydrobromic acid (1 + 9). Reserve the combined strippings for the spectrophotometric determination of iridium as in (*h*) or treat for the removal of ruthenium as in (*g*).

(*g*) *Removal of ruthenium interference before determination of iridium.* If ruthenium is present in the sample material and was not removed previously by the distillation procedure given in C10, it will accompany iridium through the TBP extraction step and subsequently interfere in the spectrophotometric determination of iridium. In such cases, treat the hydrobromic acid stripping solution with approximately 1 ml of concentrated sulphuric acid and evaporate the solution to fumes of sulphur trioxide. To volatilize ruthenium, add approximately 1 ml of concentrated perchloric acid dropwise, with swirling, to the fuming solution. After the excess of perchloric acid has evaporated, cool the solution, take up the residue in approximately 10 ml of hydrobromic acid, and boil down in a covered beaker to a small volume to ensure that iridium is present as its bromo-complex.

(*h*) *Determination of iridium.*[12,24] The reagent is a 5% solution of stannous chloride in hydrobromic acid, prepared by dissolving 12·5 g of $SnCl_2.H_2O$ in 50 ml of redistilled concentrated hydrobromic acid with gentle warming. Cool the solution to room temperature and dilute to 100 ml with water. The solution should be prepared fresh daily and should be nearly colourless immediately after preparation.

Experience has shown that, to obtain a colourless reagent solution, only clear stannous chloride crystals that dissolve readily in hydrobromic acid should be used. Stannous chloride crystals that have a dull frosted appearance and are difficultly soluble in hydrobromic acid produce an intensely coloured solution that is unsuitable as a reagent for iridium.

Transfer the hydrobromic acid solution of iridium from (*f*) or (*g*) to a 250-ml beaker and evaporate it to dryness in the presence of a few mg of sodium chloride. Add 7 ml of concentrated hydrobromic acid (which should not be coloured), cover the beaker with a watch-glass and boil the solution until it has evaporated to 2·0–2·5 ml (as judged visually, or by using comparison solution). Transfer the solution to a 25-ml volumetric flask by washing with 3 ml of concentrated hydrobromic acid and 7 ml of 25% (v/v) phosphoric acid. Place the flask in a boiling water-bath and, after 10 min, add 5 ml of stannous chloride reagent. Exactly 2 min after reagent addition, remove the flask, and cool to room temperature in a cold water-bath. Dilute the solution to the mark and measure the absorbance of the iridium complex at 402 nm against a reagent blank.

9. *Isolation and determination of osmium.* Because of the volatility of osmium compounds, the tin assay button cannot be treated by the chemical methods above to produce a solution containing osmium together with the other precious metals. Therefore osmium must be isolated directly from the tin button by distillation. The techniques for determining osmium by atomic absorption have not been established, at least in this laboratory, consequently a colorimetric method is described.

When osmium is to be determined, in copper-nickel matte for example, the sample must be fused directly, without roasting, to avoid the loss of osmium by volatilization. As indicated earlier, the other precious metals may be determined in the same assay button after distillation of osmium or, if more convenient, a separate sample may be used for their determination. Although a 25-g granulated tin button can be handled in the distillation apparatus, for simplicity and the convenience of smaller volumes, it is recommended that a 15-g portion of the tin alloy be taken for the determination of osmium whenever possible.

To distil osmium place the granulated tin button, or portion thereof, (B6) in a 500-ml distillation flask. Connect the flask to the distillation apparatus (Fig. 2) in which receivers B, C, and D contain 25, 40 and 15 ml of concentrated hydrobromic acid respectively. Receiver C is cooled in an ice-bath.

By means of a water-pump or aspirator connected to vessel D, draw air through the distillation train at the rate of 3-4 bubbles/sec. For every gram of tin alloy taken, add approximately 5 ml of 12*M* hydrochloric acid. Next, add 30% hydrogen peroxide, dropwise through the delivery tube, until the tin alloy has been decomposed and a small excess of peroxide is present. Some care must be taken during the addition of peroxide to prevent gases from sucking back up the delivery tube of the distillation head; this can be achieved by adjusting the flow of air through the distillation apparatus.

After the tin alloy has been decomposed, apply heat and evaporate the solution in the flask until its temperature rises to 115–118°. While maintaining the temperature in this range, add approximately 15 ml of 30% hydrogen peroxide in small portions in the manner described above. Next, add rapidly 30–35 ml of 12*M* hydrochloric acid through the funnel and continue the distillation until the temperature again reaches 115°. To ensure complete distillation of osmium, repeat twice more the alternate addition of 15 and 30 ml of peroxide and hydrochloric acid, respectively, with the intervening evaporations necessary to bring the temperature to at least 115° before addition of the peroxide. Do not allow the temperature to exceed 120° because higher temperatures may result in the volatilization of stannic halide.

After heating has been discontinued and the apparatus allowed to cool somewhat, disconnect the receivers and combine their contents in a 400-ml beaker containing 25 mg of sodium chloride and sufficient hydrobromic acid to make its concentration 5 *M*.

When the samples are known to contain more than 300 μg of osmium, dilute the combined receiver solutions to a known volume with hydrobromic acid and take an aliquot for the determination of osmium.

Evaporate the solution first at a low heat to prevent violent evolution of bromine; then take it to incipient dryness (without baking) at a more rapid rate. Determine the osmium content of the residue spectrophotometrically as described below.

When other precious metals in the original button are to be determined, reserve the solution remaining in the flask after the distillation of osmium and proceed with the appropriate part of the analytical scheme (Fig. 1).

When the sample is known to contain milligram amounts of native iridium–osmium alloys for example, any insoluble residue remaining in the distillation flask should be recovered by filtration and subsequently analysed for osmium by the procedures used for the first button. Experiments have shown that approximately 10% of the osmium and iridium, as intermetallic compounds of tin, may remain undissolved if the tin button is rich in these metals.

For determination of osmium the reagent is 2% pyrogallol solution prepared by dissolving 2 g of reagent-grade pyrogallol in 100 ml of distilled water containing 2 or 3 drops of 12*M* hydrochloric acid (to inhibit atmospheric oxidation). This reagent should be prepared fresh daily. A pH 2·2 buffer is also needed (prepared as in C8).

Place the hydrobromic acid solution of osmium from above (containing up to 350 μg of osmium) in a 250-ml beaker. Add 1 ml of a 2·5% sodium chloride solution and evaporate the sample just to dryness. Dissolve the salts in 10 ml of water and then add 1 ml of buffer solution (pH 2·2) and 5 ml of 2% pyrogallol solution. Using a pH meter, adjust the pH to 2·9–3·1 by the dropwise addition of a saturated solution of sodium bicarbonate. Transfer the sample solution to a 25-ml volumetric flask (without washing) and heat it in a boiling water-bath for about 30 min. The maximum colour develops within 10–15 min, but as a precaution the longer heating time is preferable. Cool the flask to room temperature (in running water) and dilute the contents to volume with water. After mixing, allow the sample to stand for 15 min and then measure its absorbance at 585 nm against either water or a reagent blank.

When less than 100 μg of osmium is to be determined, transfer the 25 ml of blue solution to a 60-ml separatory funnel and extract the osmium complex with two separate 5-ml portions of n-pentanol. Combine the extracts and centrifuge for a short time to remove water droplets. Measure the absorbance against water or a reagent blank at 585 nm, and from this determine the amount of osmium present.

Note: Ruthenium interferes in the determination of osmium. Therefore, if the solution to be analysed by the procedures given above was derived from a sample in which the ratio of ruthenium to osmium was high (*e.g.*, greater than 100, as in a precious-metals concentrate), it is recommended that the distillation of osmium be repeated to ensure that the two metals have been completely separated.

10. *Isolation of ruthenium by distillation*[13] *before colorimetric determination.*

Note: The following procedure is generally applied directly after the tin-volatilization step. However, when the sample solution contains more than about 2 g of base metals and is to be analysed subsequently for one or more of platinum, palladium, rhodium and iridium, then it is recommended that the base metals be removed by cation-exchange (C6) before the perchloric acid distillation of ruthenium. By using this approach, the subsequent task of decomposing relatively large amounts of perchlorate is avoided.

Evaporate the solution to dryness on the hot-plate to drive off as much free hydrochloric acid as possible. Cool the beaker, take up the residue in a small volume of water, and transfer to a 500-ml distillation flask by washing with several small portions of water. Connect the flask to the distillation assembly (Fig. 2) in which receiver B contains a saturated potassium permanganate solution, prepared by mixing 2 g of solid permanganate and 25 ml of water; receivers C and D contain 40 and 15 ml respectively of concentrated hydrobromic acid. Cool receiver C in an ice-bath. While air is drawn through the apparatus at the rate of 2–3 bubbles/sec, add about 50 ml of perchloric acid through the delivery funnel and apply heat to both the distillation flask and the permanganate receiver with their separate heating elements. Continue heating until the reaction mixture boils and the white fumes disappear (about 30 min). Boil the permanganate receiver solution (essentially a trap for perchloric acid) virogously until its volume is aproximately 10–15 ml; then shut off, and remove, the heating mantle.

Combine the hydrobromic acid receiver solutions, treat with about 25 mg of sodium chloride, and

TABLE I.—COMPARATIVE RESULTS FOR PRECIOUS METAL-BEARING SAMPLES (CONCENTRATIONS IN ppm)

Sample		Pt	Pd	Rh	Ir	Ru	Os	Au	Ag
South African head ore	Proposed methods	4·5	2·0	0·3	—	—	—	0·4	0·7
	Mean of results from four independent laboratories*	4·8	2·1	0·3	—	—	—	0·4	0·7†
Cu-Ni Matte No. 1	Proposed methods	5·2	5·1	1·8	$0{\cdot}8_6$	1·5	0·3	2·0	—
	Independent labs.[10–14]	5·3	5·1	1·9	$0{\cdot}8_4$	1·4		2·2	—
Cu-Ni Matte No. 2	Proposed methods[27]	5·5	6·0		0·9	1·4	0·3	1·9	
	Independent lab. A[27]	5·5	5·1		0·8	1·4		2·0	
	Independent lab. B[27]	6·2	5·2		0·9	1·5	0·3	1·8	
Flotation Conc., Sudbury, Ont.	Proposed methods	$0{\cdot}8_5$	$0{\cdot}7_0$	0·3	0·1	0·3	—	$0{\cdot}6_5$	18
	Independent lab.[10,11,14]	$0{\cdot}8_5$	$0{\cdot}7_5$	0·3	—	—	—	$0{\cdot}6_2$	19‡
Black Sands Conc., Tulameen, B.C.	Proposed methods	3·1							2·0
	Mean of results from four independent laboratories*	3·0							1·7§
Precious Metals Conc. (refinery product)	Proposed methods	1·23%	1·70%	5·48%	2·94%	4·64%	—%	0·28%	19·4%
	Independent lab.[28]	1·21%	1·72%	5·56%	2·78%	4·72%	—%	0·26%	19·8%

* Results obtained in unpublished interlaboratory study.

† Average of results from two laboratories only.

‡ Average of results of two methods (private communication to authors).

evaporate the whole solution or an aliquot, just to moist salts, before the spectrophotometric determination of ruthenium with *p*-nitrosodimethylaniline.[26]

To remove perchloric acid (only after ruthenium distillation), transfer the perchloric acid solution from the ruthenium distillation to a 600-ml beaker and heat strongly to drive off as much free perchloric acid as possible. Stir the residue with a small volume of 6*M* hydrochloric acid and again evaporate to dryness. Repeat these operations until most of the perchlorates have been destroyed (as evidenced by the absence of white fumes).

To ensure that the platinum metals are in a soluble form, treat the residue with approximately 15 ml of *aqua regia*, heat, and evaporate to dryness in a covered beaker. Remove the watch-glass and, by repeated additions of 12*M* hydrochloric acid and subsequent evaporations, convert the metals into their chloro-salts. Analyse the solution for their precious metals content by the procedure described above.

RESULTS

Table I presents results obtained by the proposed tin-collection scheme of analyses on a number of materials. It is apparent that these are in relatively good agreement with analyses obtained by independent laboratories which, collectively, used a wide variety of methods.

Acknowledgement—We are grateful to the American Chemical Society (the copyright holder) for permission to reprint Fig. 2 and to quote from various papers[10-14,20,25] published in *Analytical Chemistry*.

Zusammenfassung—Ein umfassendes Analysenschema zur Bestimmung der sechs Metalle der Platingruppe sowie von Gold und Silber wird angegeben. Es besteht in der Vereinigung einzelner Verfahren, die teilweise im Laufe mehrerer Jahre schon beschrieben wurden. Das Analysenschema wurde in Schieds- und Standardanalysen an einer großen Vielfalt von Material überprüft und ist folglich von zunehmendem Interesse für viele Laboratorien. Die Probe wird bei 1200–1250° mit einem Schmelzfluß aus Zinndioxid, Natriumcarbonat, Kieselsäure, Borax und Kokspulver geschmolzen; dabei sammeln sich die Edelmetalle im geschmolzenen Zinn an. Die erhaltene Zinnlegierung wird gelöst und die Edelmetalle durch Ionenaustausch-, Extraktions- und Destillationsverfahren isoliert. Mit Ausnahme der für den Schmelzaufschluß notwendigen Einrichtungen kann man bei den naßchemischen Operationen zur Isolierung und Bestimmung der einzelnen Edelmetalle herkömmliches Gerät verwenden.

Résumé—On présente un schéma analytique complet pour le dosage des six métaux du groupe du platine, de l'or et de l'argent. Il est le résultat de l'intégration de techniques séparées qui ont été décrites antérieurement, en partie, dans le courant de plusieurs années. Le schéma analytique a été totalement mis à l'épreuve sur une large variété de produits par un travail arbitré et normalisé et, en conséquence, il est d'un intérêt croissant pour de nombreux laboratoires. Les métaux précieux sont rassemblés dans de l'étain fondu lorsque l'échantillon est fondu à 1200°–1250° avec un fondant contenant de l'oxyde stannique, du carbonate de sodium, de la silice, du borax et de la farine. L'alliage d'étain résultant est dissous et les métaux précieux sont isolés par des techniques d'échange d'ions, d'éxtraction par solvant ou de distillation. A l'exception des conditions usuelles requises au stade de la fusion de l'essai par voie sèche, l'équipement type peut être utilisé dans les opérations chimiques par voie humide pour l'isolement et le dosage des différents métaux précieux.

REFERENCES

1. I. Hoffman, A. D. Westland, C. L. Lewis and F. E. Beamish, *Anal. Chem.*, 1956, **28**, 1174.
2. J. G. Fraser and F. E. Beamish, *ibid.*, 1954, **26**, 1474.
3. W. F. Allen and F. E. Beamish, *ibid.*, 1950, **22**, 451.
4. R. R. Barefoot and F. E. Beamish, *ibid.*, 1952, **24**, 840.
5. R. Theirs, W. Graydon and F. E. Beamish, *ibid.*, 1948, **20**, 831.

6. W. J. Allan and F. E. Beamish, *ibid.*, 1952, **24**, 1569.
7. F. E. Beamish, *Talanta*, 1960, **5**, 1.
8. *Idem, ibid.*, 1959, **2**, 244.
9. G. H. Faye, *Mines Branch Res. Rept.*, R 154, Dept. Energy, Mines and Resources, Ottawa, Canada, 1965.
10. G. H. Faye and W. R. Inman, *Anal. Chem.*, 1961, **33**, 278.
11. *Idem, ibid.*, 1962, **34**, 972.
12. G. H. Faye, W. R. Inman and P. E. Moloughney, *ibid.*, 1964, **36**, 366.
13. G. H. Faye, *ibid.*, 1965, **37**, 696.
14. G. H. Faye and W. R. Inman, *ibid.*, 1961, **33**, 1914.
15. P. E. Moloughney and J. A. Graham, *Talanta*, 1971, **18**, 475.
16. H. G. Coburn, F. E. Beamish and C. L. Lewis, *Anal. Chem.*, 1956, **28**, 1297.
17. A. G. Marks and F. E. Beamish, *ibid.*, 1958, **30**, 1464.
18. H. Zachariasen and F. E. Beamish, *ibid.*, 1962, **34**, 965.
19. M. M. Schnepfe and F. S. Grimaldi, *Talanta*, 1969, **16**, 891.
20. G. H. Faye and W. R. Inman, *Anal. Chem.*, 1963, **35**, 985.
21. J. H. Yoe and J. J. Kirkland, *ibid.*, 1954, **26**, 1335.
22. G. H. Ayers and A. S. Meyer, Jr., *ibid.*, 1951, **23**, 299.
23. S. S. Berman and R. Ironside, *Can. J. Chem.*, 1958, **36**, 1151.
24. S. S. Berman and W. A. E. McBryde, *Analyst*, 1956, **81**, 566.
25. G. H. Faye, *Anal. Chem.*, 1965, **37**, 259.
26. J. E. Currah, A. Fischel, W. A. E. McBryde and F. E. Beamish, *ibid.*, 1952, **24**, 1980.
27. J. H. Crocket, R. R. Keays and S. Hsieh, *J. Radioanal. Chem.*, 1968, **1**, 487.
28. H. Zachariasen and F. E. Beamish, *Talanta*, 1960, **4**, 44.

Talanta, 1972, Vol. 19, pp. 285 to 292. Pergamon Press. Printed in Northern Ireland

KINETIC METHOD OF ANALYSIS BY ANALOGUE COMPUTER SIMULATION

MASAKI NAKANISHI
Department of Chemistry, Ochanomizu University
Bunkyo-ku, Tokyo, Japan

(*Received* 15 *July* 1971. *Accepted* 15 *September* 1971)

Summary—The simulation by an analogue computer of slow reactions used for the purpose of chemical analysis is described. Bromination of maleic and fumaric acids is used for illustration. The concentration of bromine is traced spectrophotometrically as a function of time and the trace simulated with an analogue computer by the trial and error method. The initial concentration of the substance in question and the rate constant of the reaction are determined from the values given to the computer variables to obtain the best fit. Only a single experiment is required for the analysis. The procedure can be followed easily without laborious mathematical or graphical treatment.

KINETIC methods of chemical analysis have been applied successfully to a number of inorganic and organic substances. In spite of various advantages, the methods are hardly general and only restricted applications have been reported. Most of the reactions employed are first-order or pseudo first-order (*viz.* a second-order reaction, with a large excess of one reactant). When a mixture of two unknown components is to be analysed, it is usually a prerequisite that the sum of the concentrations of the two components is known or that the rate constants are considerably different from each other. Sometimes the rate constant involved in the particular reaction has to be determined in a separate run under rigorously controlled experimental conditions. In addition, the majority of the methods proposed require a rather laborious graphical or mathematical treatment of the results.

A differential equation expressing a kinetic reaction can be most readily solved graphically by means of an analogue computer. Although little use has been made of the analogue computer technique in chemical problems, some successful applications to the study of reaction kinetics of a complex system have been demonstrated.[1-4]

In these studies the technique was employed mostly to determine the rate constant and the order of reaction by the simulation method, but it also offers a means of determining the reacting component in the system. It should be faster and easier to use than graphical methods.

In this paper, the application of an analogue computer to chemical analysis is described. Simple bromination reactions of unsaturated compounds, maleic and fumaric acids, which obey second-order kinetics, have been selected and the processes followed spectrophotometrically. Reaction kinetic methods which employ bromination reactions to determine organic unsaturation have been reported previously.[5-8] In this earlier work extensive graphical or mathematical treatment of the results was important, but in this study the absorbance curve of the reacting mixture as a function of time is simulated with an analogue computer by a curve-fitting procedure and the initial concentration of the sample compound is determined from the machine variable. It is to be expected that even if the reaction proceeds slowly and a relatively long time is required before completion, observation of only the initial stage of reaction will suffice for the simulation. As is evident in the following section, the method is applicable without modification to a system in which the concentration of the sample substance is equal to that of the bromine.[9]

THEORY

Throughout this work a reaction between substances A and B which obeys second-order kinetics is considered:

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{1}$$

where t is time in sec, k is the rate constant in l.mole^{-1}.sec^{-1}, a and b are the concentrations in mole.l.$^{-1}$ of substances A and B, respectively, at $t = 0$, and x is the amount of the substances consumed in time t, expressed in concentration units. A is supposed to be the substance to be determined and B is the reactant added.

If the concentration of B could be followed by any means during the course of reaction, a curve showing the variation of $(b - x)$ as a function of time would be obtained.

On the other hand, the differential equation (1), the so-called physical equation expressing the real physical phenomenon, or the chemical reaction could be simulated with an analogue computer. As a result, a curve entirely identical in shape and magnitude with the experimental curve, $(b - x)$ *vs.* t, could be reproduced on the computer output as a function of the machine time T. The circuit diagram relevant to equation (1) is shown as a block scheme in Fig. 1. The voltages shown are those that appear at any part of the circuit at time t when known voltages $-A$ and $-B$ are applied to the adders II and III, respectively, and the circuit is closed at $t = 0$.

The analogue computer circuit represents the following so-called machine equation:

$$\frac{dX}{dT} = \frac{K}{10}(A - X)(B - X) \tag{2}$$

where T is the machine time and the coefficient $K/10$ originates from the characteristics of the multiplier that the output voltage is a tenth of the product, with inverted sign, of two input voltages.

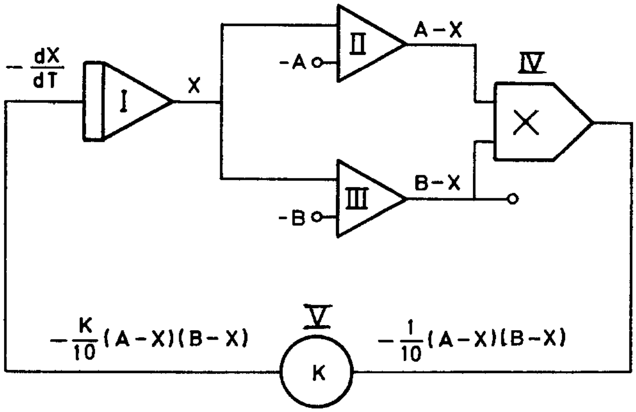


FIG. 1.—Analogue computer circuit diagram for the second-order reaction (1).
I, integrator; II, III, adders; IV, function multiplier; V, coefficient potentiometer.

The voltage $(B - X)$ that appears at the output of the adder III as a function of T can be obtained as a curve on a recorder. This fits with the experimental curve $(b - x)$ *vs.* t, as is evident from the similarity of equations (1) and (2), provided certain relationships [equations (3) and (6) below] hold.

Because curves fit at $t = 0$, at which $x = 0$, the following relationship is valid:

$$B = \alpha b \tag{3}$$

where α is a conversion factor in V.l.mole^{-1}. Consequently, fitting at any point of the curves leads to the expressions,

$$X = \alpha x \tag{4}$$

$$A = \alpha a \tag{5}$$

Also T is related to t by the equation

$$T = \beta t \tag{6}$$

where β is a conversion factor.

Thus, equation (2) can be rewritten as

$$\frac{dx}{dt} = \frac{\alpha \beta K}{10}(a - x)(b - x) \tag{7}$$

Because the two curves fit, equation (7) should be identical with equation (1). Hence,

$$k = \frac{\alpha \beta K}{10} \tag{8}$$

In conclusion, if the two curves which correspond to the physical and machine equations fit each other, the initial concentration, a, of the substance A and the rate constant, k, can be obtained from (5) and (8), respectively.

EXPERIMENTAL

Apparatus

Spectrophotometer. Hitachi, Model 101-003. To accommodate a reaction vessel in the cell compartment and agitate a solution inside the vessel with a magnetic stirrer, the cell compartment was reconstructed with aluminium plates lined with dark woollen cloth. A magnetic stirrer was placed immediately under the cell compartment. The case plates of the spectrophotometer were removed as a precaution to avoid accumulation of heat inside the compartment.

The reaction vessel was a 100-ml cylindrical glass vessel which was fitted with a silicone rubber stopper and placed in the cell compartment as shown in Fig. 2. Two Teflon strips were attached to the stopper to prevent the solution from forming a convex surface. A deep hole was bored in the stopper so that a layer that could be punctured with a needle was left at the bottom of the stopper. Correspondingly, a hole was drilled in the lid of the compartment and covered with dark woollen cloth. A vinylidene chloride sheet was placed between the stopper and the glass vessel to avoid the reaction of bromine with the stopper material.

The electrical output of the spectrophotometer, proportional to the transmittance and having a value of 10 mV at 100% transmittance, was amplified by a factor of slightly over 100 with an amplifier, Model PM-17A, Toa Electronics, of which the output voltage was attenuated to exactly 1.000 V for 100% transmittance. The overall drift in several hours amounted to less than 1% transmittance.

Values of transmittance thus obtained were converted into absorbance by means of a logarithmic converter which was constructed in the author's laboratory from a logarithmic module, Model LGP-3, and operational amplifiers, Models SA-3a and SQ-10a, supplied by Philbrick/Nexus. A detailed description of the circuitry is omitted, but it provided logarithmic output voltages of 0·00 and 1·00 V for input voltages of 0·100 and 1·000 V, respectively. The working range covered approximately two decades.

The absorbance value was recorded on a 2-pen potentiometric recorder, Model EPR-3T, Toa Electronics. The absorbance estimated on the trace was precise to 0·002.

The syringe pipette for delivering sample solutions through the hole in the rubber stopper was a 250-μl Hamilton syringe. Water was used for calibration.

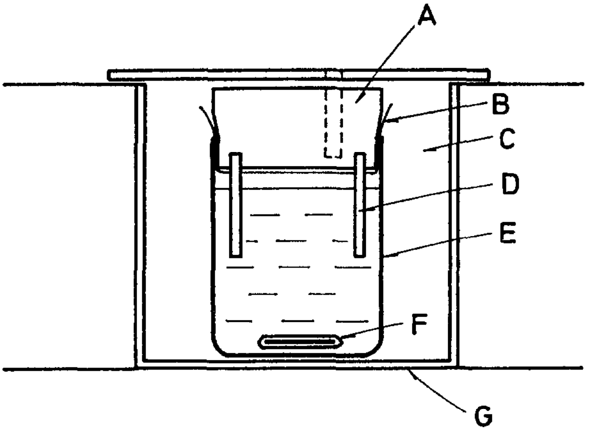


FIG. 2.—Reaction vessel and cell compartment.
A, silicone rubber stopper; B, vinylidene chloride sheet; C, cell compartment; D, Teflon strip; E, reaction vessel; F, stirrer rod; G, aluminium plate.

Analogue computer. This was also constructed in the author's laboratory. A Philbrick/Nexus operational amplifier SA-3a was used for the integrator and SQ-10a operational amplifiers for adders. A Burr-Brown Model 4030/25 quarter-square multiplier was used for the function multiplier and a Beckman-Toshiba Helipot, 10 kΩ, for the coefficient potentiometer. The capacitor was a 10-μF sintered anode solid electrolytic tantalum condenser, J5NSSA, Nippon Chemical Condensers. Resistors were commercially available 5%-grade products. The performance of the analogue computer was tested on an individual-parts basis, and the corrections thus obtained were applied to the final evaluations of concentration of the sample substance and the rate constant.

Reagents

All reagents used were of guaranteed grade. Allyl alcohol was distilled and the 95–97° fraction was used. Solutions were made up with distilled water except for the ethanolic solution of allyl alcohol. Accurate concentrations were calculated from the weight of solute and the volume. A blank test was carried out with respect to bromine consumption for each run before a sample solution was added.

Procedure

Calibration graph of bromine concentrations. The concentration of bromine was determined from the absorbance of the solution. A known volume (90 ml for the particular reaction vessel used) of 0·05*M* potassium bromide adjusted to pH 4·2 with acetic acid–acetate buffer was placed in the reaction vessel shown in Fig. 2. This was then settled in the cell compartment. An arbitrary amount of bromine was added through the lid of the compartment and the rubber stopper by use of a syringe pipette, while the solution was being stirred with a magnetic stirrer. The absorbance, A_0, of the resulting solution was measured at 370 nm against a blank solution. A known amount of allyl alcohol was then added in the same manner with a syringe pipette, and the absorbance, A, was measured. The decrease in the concentration of bromine due to the fast reaction with allyl alcohol could be calculated from the amount of allyl alcohol added, an equimolar reaction being assumed. With the amount of allyl alcohol expressed in terms of concentration, C, a plot of A_0 against $CA_0/(A_0 - A)$ for different values of A_0 and different amounts of allyl alcohol gave a straight line, which showed the relationship between concentration and absorbance of the bromine solutions in the particular vessel.

No particular effort was made to maintain a constant temperature in the solution under reaction, because the primary object was not the determination of the rate constant. Nevertheless, the temperature was essentially constant during the several minutes of the reaction period.

RESULTS AND DISCUSSION

Analytical bromination of unsaturated compounds has been carried out mainly under strongly acid conditions, to prevent hydrolysis of bromine.[10–12] However, in such an acid solution the bromination reactions of maleic and fumaric acids proceed much more slowly than those of the corresponding ionic species.[6,13] Since the hydrolysis of bromine did not substantially occur at pH below 4.5, for this work pH 4.2 was selected and maintained with an acetic acid–acetate buffer.

Several precautions had to be taken against the loss of bromine. It could be considerably reduced by adding potassium bromide to the solution to give the less volatile tribromide ion species. Also the volume of solution in the reaction vessel should be increased so as to minimize the space above the solution, since it was found that the absorbance of the solution continued to decrease until the head-space was saturated with bromine vapour. Continuous stirring of the solution accelerated volatilization, and it took 10 min at most before the decrease in absorbance substantially ceased.

The aqueous bromine solution has a maximum absorption at 390 nm whilst that of the tribromide ions is at a much shorter wavelength, so a solution containing both bromine and potassium bromide shows a plateau on its absorbance curve between 360 and 380 nm. For this reason the absorbance was measured at 370 nm.

The three bromine species, Br_2, Br^- and Br_3^-, are connected by the relationship

$$Br_2 + Br^- \rightleftharpoons Br_3^- \tag{9}$$

Each of them may take part in the bromination of maleic and fumaric acids, and therefore should be taken into consideration, although the participation of tribromide ions in the bromination reactions of 8-quinolinols[4] and phenetole[10] is unimportant. However, when the concentration of potassium bromide is large enough, as in the present work, the ratio of $[Br_2]$ to $[Br_3^-]$ remains substantially constant. As a result, total possible participation of the three species in the reaction kinetics is considered to be proportional to the concentration of Br_2, or to the absorbance measured at 370 nm.

To achieve the most reliable fit of the two traces, a sufficiently curved trace of absorbance was desired, since prominently curved traces are more easily checked for congruence. Consequently, it was better, with a slow chemical reaction, to reduce the chart speed. The analogue computer trace could be more rapidly drawn by using a value of β less than unity.

Another important factor for obtaining a trace of larger curvature is the ratio of the initial concentrations of reacting substances, b/a. The effect of the ratio b/a on the curve shape will be discussed in terms of the reaction of fumaric acid with bromine.

Initial portions of the absorbance traces, $(b - x)$ *vs.* t, for a certain constant value of a and different values of b/a are shown in Fig. 3. The curves are arbitrarily displaced along the ordinate axis only to illustrate the curvature of the traces. The rate constant and the time scale, which are related to each other according to equation (8), are not referred to since they are unimportant in this discussion.

Curve I, for which the ratio b/a is 5, is sufficiently curved to be useful, but poor curvature results for smaller values of b/a, even when a more sensitive recorder range is used. Thus a higher concentration ratio of bromine to unsaturated compound is preferable.

However, when traces from larger values of b/a were still not sufficiently curved, the curvature could be emphasized if a certain constant voltage was subtracted from the trace at the input of the recorder and the remainder was recorded in a more sensitive range. The effect of this differential procedure on the curve shape is apparent

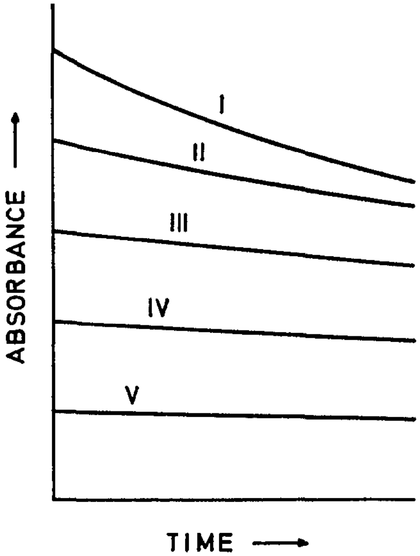


FIG. 3.—Dependence of the initial portion of absorbance trace, $(b - x)$ *vs.* t, on the ratio b/a, when a and k remain constant.
Values of b/a: I, 5; II, 2; III, 1; IV, $\frac{1}{2}$; V, $\frac{1}{5}$.

in Fig. 4. Curves I′, III′ and V′ represent magnification of the traces I, III and V in Fig. 3 from which 80% of the initial absorbance has been subtracted. The curves were drawn at sensitivities 2·5, 10 and 25 times those used for the respective traces in Fig. 3. The curvature of V′ is still poor, but the pronounced curvature of I′ and III′ permitted the method to be applied to a relatively slower reaction.

The initial concentration of bromine, b, in the real chemical experiment could be determined from the absorbance before addition of sample. The corresponding value, B, to be given to the analogue computer might be decided arbitrarily, and would determine α in equation (3).

The values of A and K needed to give exact fit of the machine curve with the experimental curve gives the values of a and k, according to equations (5) and (8). However, small changes in A and K might produce no appreciable effect on the machine curve, if the changes compensated each other. Thus, the graphical simulation method gives ranges of A and K instead of definite values. This is the most serious limitation to the precision of the method.

The most probable values of a and k were estimated as the mid-point of the ranges a and k thus obtained, and the precision was taken as half the range.

Maleic acid in aqueous solutions of different concentrations was treated at room temperature by the proposed method. Although the temperature was not controlled, it remained substantially constant during each run. Results are shown in Table I. The results seem to be tolerable, but errors as great as $0{\cdot}1 \times 10^{-4}$ mole.l.$^{-1}$ may occur. The temperature ranged from 19 to 23° for different runs. However, the estimated values of rate constant were apparently not correlated with the temperature.

The reaction of fumaric acid with bromine required a longer time to produce a sufficiently curved trace on a recorder owing to the lower rate of reaction. A lengthy experiment is undesirable, not only for reasons of time but also because of increased loss of bromine by volatilization. Consequently, to obtain well-curved traces, about

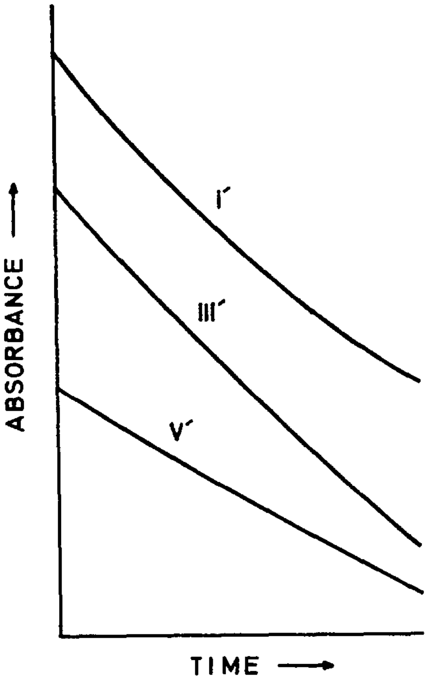


FIG. 4.—Magnification of the curves I, III and V in Fig. 3. Values of b/a: I′, 5; III′, I; V′, $\frac{1}{5}$.

TABLE I.—DETERMINATION OF MALEIC ACID

Concentration of maleic acid, 10^{-4} *mole.l.*$^{-1}$		Rate constant, *k*, *l.mole*$^{-1}$*.sec*$^{-1}$
Calc.	Found	
1·03	1·04 (±0·04)	9·2 (±0·6)
1·54	1·54 (±0·05)	8·4 (±0·4)
1·67	1·73 (±0·06)	8·9 (±0·5)
2·05	1·95 (±0·08)	7·7 (±0·5)
2·50	2·41 (±0·07)	9·0 (±0·4)
2·56	2·57 (±0·07)	8·6 (±0·6)
3·34	3·39 (±0·07)	8·0 (±0·3)
4·17	4·09 (±0·12)	8·6 (±0·5)

80% of the voltage was subtracted at the input of the recorder by applying a negative voltage and the remaining input was recorded at higher sensitivity. The same treatment was applied to the simulation process. Thus, a voltage α times as large as the subtracted voltage was subtracted from the analogue computer output and the resulting trace was used to find appropriate values of A and K.

Some examples of the kinetic analysis of fumaric acid are shown in Table II. The differences between the calculated and experimental values are tolerable, but the precision is poorer than for maleic acid, probably because of the more complex procedure.

Advantages of the proposed method are the ease with which the experimental results can be treated without laborious mathematical or graphical treatment, that

TABLE II.—DETERMINATION OF FUMARIC ACID

Concentration of fumaric acid, 10^{-4} *mole.l.*$^{-1}$		Rate constant, *k*, *l.mole*$^{-1}$*.sec*$^{-1}$
Calc.	Found	
2·56	2·59 (±0·15)	2·0 (±0·2)
3·38	3·38 (±0·27)	2·0 (±0·2)
4·19	4·27 (±0·42)	1·8 (±0·2)

only a single experiment is needed and that the nature of the reaction and the substances involved need not be known except for the type of differential equation which represents the kinetics of the reaction. Conversion of the time scale, as expressed by equation (6), is an additional feature of the method, by use of which results for a slow reaction could be treated in a shorter time.

Application of the method is not restricted to second-order kinetics nor to a spectrophotometric process. Extension of the method to a mixed component system is also promising.

Acknowledgement—I would like to thank Miss Yumiko Masaki for her helpful collaboration.

Zusammenfassung—Die Simulierung langsamer Reaktionen, die man zur chemischen Analyse verwerten kann, mit Hilfe eines Analogrechners wird beschrieben. Als Beispiel wird die Bromierung von Malein- und Fumarsäure angeführt. Die Bromkonzentration wird spektrophotometrisch in Abhängigkeit von der Zeit verfolgt und die Registrierkurve nach einem trial-and-error-Verfahren mit dem Analogrechner simuliert. Die Anfangskonzentration der zu bestimmenden Substanz und die Geschwindigkeitskonstante der Reaktion werden aus den Werten berechnet, die man dem Rechner eingegeben hat, um die beste Übereinstimmung zu erzielen. Für die Analyse wird nur ein Experiment benötigt. Man kann dem Verfahren ohne großen mathematischen oder graphischen Aufwand leicht folgen.

Résumé—On décrit la simulation par une calculatrice analogique de réactions lentes utilisées en vue d'analyse chimique. On utilise la bromuration des acides maléique et fumarique comme illustration. La concentration du brome est tracée spectrophotométriquement en fonction du temps et le tracé simulé avec une calculatrice analogique par la méthode des approximations successives. La concentration initiale de la substance en question et la constante de vitesse de la réaction sont déterminées à partir des valeurs données aux variables de la calculatrice pour obtenir le meilleur degré d'accord. Une seule expérience est nécessitée pour l'analyse. La technique peut être suivie aisément sans traitement mathématique ou graphique laborieux.

REFERENCES

1. H. B. Mark, Jr., L. J. Papa and C. N. Reilley, *Advan. Anal. Chem. Instrumentation*, 1963, **2**, 368.
2. J. Janata and O. Schmidt, *J. Electroanal. Chem.*, 1966, **11**, 224.
3. J. Janata, O. Schmidt and P. Zuman, *Collection Czech. Chem. Commun.*, 1966, **31**, 2344.
4. G. O'Dom and Q. Fernando, *Anal. Chem.*, 1966, **38**, 844.
5. J. W. Miller and D. D. DeFord, *ibid.*, 1957, **29**, 475.
6. S. Siggia, J. G. Hanna and N. M. Serencha, *ibid.*, 1963, **35**, 362.
7. J. G. Hanna and S. Siggia, *ibid.*, 1965, **37**, 690.
8. J. S. Fritz and G. E. Wood, *ibid.*, 1968, **40**, 134.
9. C. N. Reilly and L. J. Papa, *ibid.*, 1962, **34**, 801.
10. G. S. Kozak and Q. Fernando, *J. Phys. Chem.*, 1963, **67**, 811.
11. G. S. Kozak, Q. Fernando and H. Freiser, *Anal. Chem.*, 1964, **36**, 296.
12. G. O'Dom and Q. Fernando, *ibid.*, 1965, **37**, 893.
13. F. E. Critchfield, *ibid.*, 1959, **31**, 1406.

Talanta, 1972, Vol. 19, pp. 293 to 298. Pergamon Press. Printed in Northern Ireland

MÖGLICHKEITEN UND GRENZEN BEI DER VERWENDUNG VON FILTERPAPIER ALS TRÄGER BEI DER RÖNTGENSPEKTROMETRISCHEN ANALYSE

G. Ackermann, R.-K. Koch,[1] H. Ehrhardt und G. Sanner
Bergakademie Freiberg, Sektion Chemie—Lehrstuhl für Analytische Chemie

und

VEB Bergbau und Hüttenkombinat "Albert Funk"—Forschungsinstitut für NE-Metalle, Freiberg (Sachs), DDR

(*Eingegangen am* 20. *August* 1970. *Revidiert am* 4. *Mai* 1971. *Angenommen am* 13. *September* 1971)

Zusammenfassung—Die Untersuchungen haben gezeigt, daß sich Filterpapier als Trägermaterial für die Röntgenfluoreszenz-Analyse prinzipiell eignet und daß man bei Einsatz der Ringofen-Technik nach Weisz eine hohe Empfindlichkeit bei einer hinreichend reproduzierbaren Probengeometrie erreichen kann. Die Konzentrations-Intensitätsbeziehungen sind für Ag, Pd, Rh, Pt, Au, Cu, Fe und Ca im Bereich von 0 bis 100 μg linear. Die relativen Standardabweichungen schwanken bei Gegenwart aller Elemente zwischen 7 und 30%, die Nachweisgrenzen liegen zwischen 8 μg/ml (für Eisen) und 35 μg/ml (für Calcium). Die Arbeitszeit beträgt für 5 Parallelproben *ca.* 30 min. Mit Hilfe der Wachsringtechnik läßt sich bei vergleichbarer Reproduzierbarkeit der Meßwerte, allerdings bei verringerter Empfindlichkeit, die Analysendauer auf etwa 15 min senken.

Da bei manchen Röntgenspektrometern die direkte Analyse von Flüssigkeiten wegen ungünstiger geometrischer Anordnung des Probenhalters Schwierigkeiten bereitet, verwendet man Trägermaterialien zur Fixierung solcher Proben. Sowohl bei der Untersuchung von Lösungen als auch bei der Verwendung von Trägern hat man den Vorteil, daß sich die Eichproben verhältnismäßig einfach präparieren lassen und die Verwendung innerer Standards kaum Mühe macht. Als Trägermaterialien werden in der Literatur z.B. Cellulose, PVC-Pulver, Polyäthylenpulver usw. empfohlen.

Als besonders zweckmäßig hat sich Cellulose, sowohl in Pulverform wie auch als Filtrierpapier erwiesen. Bei Einsatz von Papier erscheint zur Konzentrierung der Probe und damit zur Erhöhung der Meßempfindlichkeit die Kombination mit der Ringofentechnik nach Weisz[2] besonders empfehlenswert. Erstmalig ist darüber von Püschel[3] berichtet worden. Der Autor stellt fest, daß Filtrierpapier als organische Matrix eine geringe Untergrundstrahlung liefert und infolge seiner Saugfähigkeit eine genügend große Aufnahmefähigkeit für die zu untersuchende Lösung aufweist. Auch die Oberflächenbeschaffenheit und seine mechanische Widerstandsfähigkeit lassen es als Träger für röntgenspektrometrische Untersuchungen geeignet erscheinen. Über eine Kombination von Röntgenspektroskopie und Ringofentechnik berichten u.a. nach Natelson und Sheid,[4] die auf diesem Wege kleine Calcium-Mengen bestimmten.

Ziel der Untersuchungen war es, den Einsatz der Ringofentechnik zur Probenvorbereitung für die röntgenspektrometrische Bestimmung von Palladium, Rhodium, Gold und Platin neben Silber, Kupfer, Eisen und Calcium zu prüfen.

EXPERIMENTELLER TEIL

Meßbedingungen

Einkanalvakuum-Röntgenspektrometer "Fluroprint" V150 (Hilger und Watts, London)
Anregungsbedingungen: 50 kV, 30 mA; W-Anode
Analysatorkristall: LiF
Kollimator: 0,25 mm
Impulsvorwahl: 10^5 Imp. (für Ca-$K_{\alpha 1,2}$: $3 \cdot 10^5$ Imp.)
Probekammer: Titaneinsatz
Probehalterung: PVC-Block
Chromatographiepapier: FN 15 des VEB Spezialpapierfabrik Niederschlag
Probendurchmesser: 18 mm

Probenpräparation

Auf einem Ringofen, dessen Bohrung den Abmessungen des Fensters im Spektrometer angepaßt ist, wird das gewünschte Volumen der Probelösung eingedampft. Dabei ist darauf zu achten, daß der vorgegebene Ring-Durchmesser nicht überschritten wird. Es ist aber nicht erforderlich, daß die gesamte Menge in dem Ring konzentriert wird.

Eichreihen der reinen Lösungen

Vorversuche dienten zur Aufnahme der Eichkurven für die reinen Komponenten, von denen der Bereich von 0 bis 100 μg/ml geprüft wurde. Man erhält bei allen untersuchten Elementen für die Konzentrations-Intensitäts-Beziehung Geraden mit unterschiedlichem Anstieg. Die Anstiegsfaktoren sind in Tabelle I zusammengefaßt.

TABELLE I.—ANSTIEGSFAKTOREN DER EICHGERADEN UND NACHWEISGRENZEN FÜR DEN BEREICH 0–100 μg DER GEPRÜFTEN ELEMENTE

Element	Ca	Fe	Cu	Au	Pt	Rh	Pd	Ag
Anstieg	0,90	0,76	0,49	0,17	0,15	0,11	0,10	0,06
Nachweisgrenze, *μg/ml*	35	8	13	22	37	24	27	31

Eichreihen für die Mehrkomponentengemische

Unter Verwendung entsprechender Stammlösungen wurden im Bereich von 0 bis 100 μg über die Meßpunkte 0, 5, 25, 50, 75 und 100 μg für jedes Element Eichkurven aufgenommen, bei denen die Begleitelementmatrix, bestehend aus weiteren 6 Elementen, in 3 Stufen (1, 50 und 100 μg) zugemischt wurde. Der Gehalt an Matrix blieb dann für die ganze Reihe konstant.

Durch Vergleich mit den Meßwerten für die reinen Lösungen kann dann auf den Einfluß der Matrixelemente geschlossen werden. Als Beispiel zeigt Abb. 1 das Verhalten von Eisen in einer reinen Lösung und in Gegenwart von je 50 und 100 μg des Gemisches der Matrixelemente. Es ist zu erkennen, daß der Anstieg der Eichgeraden erwartungsgemäß vom Gehalt an Matrixelementen beeinflußt wird. Um Schwankungen durch die Meßanordnung zu beseitigen, sind die Messungen mit äußerem Standard vorgenommen worden.

Um die Interelementeffekte zu verringern, arbeitet man häufig mit einem inneren Standard. Für unsere Messungen bot sich dazu Zink an. Als Beispiel sind in Tabelle II die Anstiegsfaktoren fur die Bestimmung von Eisen in Gegenwart der Begleitelemente zusammengestellt. Man sieht deutlich, daß Zink als Standard geeignet ist, weil durch dessen Zusatz der Einfluß der Partner auf die Meßwerte vermindert wird.

TABELLE II.—WIRKUNG VON ZINK ALS INNERER STANDARD BEI DER BESTIMMUNG VON 0 BIS 25 μg EISEN

	Anstiegsfaktoren
Innerer Standard ohne Begleitelemente	0,46
Äußerer Standard ohne Begleitelemente	0,37
Äußerer Standard mit Begleitelemente	0,28

Für Palladium und Rhodium erzielten wir durch Verwendung des Untergrundes als inneren Standard sehr günstige Ergebnisse. Dieses Verfahren hat noch den Vorteil, daß ein zusätzlicher Zeitaufwand für das Zumischen der Bezugslösung entfällt.

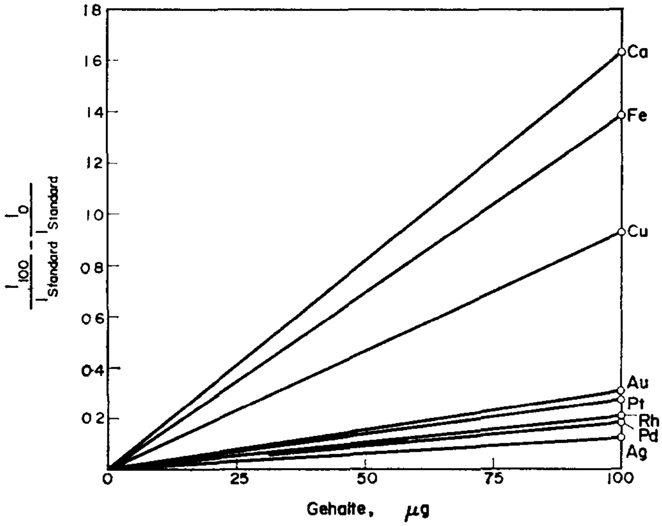


ABB. 1.—Eichkurven für die Bestimmung von Silber, Palladium, Rhodium, Platin, Gold, Kupfer, Eisen und Calcium

DISKUSSION DER ERGEBNISSE

Reproduzierbarkeit und Nachweisgrenzen

Um den durch das Spektrometer hervorgerufenen Meßfehler zu erfassen, wurden von jedem Element bei einer mittleren Menge von der gleichen Probe 11 (bzw. 10) Messungen durchgeführt. Wie Tabelle III zeigt, liegen die Variationskoeffizienten für die einzelnen Elemente zwischen 1,0 und 5,5%.

Um den Einfluß der Probenvorbereitung mit zu erfassen, sind (in Gegenwart aller anderen genannten Elemente) jeweils an 11 (bzw. 10) individuellen Proben bei einer mittleren Menge Messungen vorgenommen worden. Die Ergebnisse enthält Tabelle IV. Aus den zwischen 6,8 und 23% liegenden Variationskoeffizienten kann man ableiten, daß zur Erhöhung der Präzision der Messungen die Präparationstechnik vervollkommnet werden muß.

Wie Tabelle I zeigt, liegen die aus statistischen Berechnungen[6] für Pd und Pt bzw. aus den Regressionsgeraden[6] für alle anderen Elemente berechneten Nachweisgrenzen zwischen 8 µg/ml (Eisen) und 35 µg/ml (Calcium). Durch Verwendung eines inneren Standards können diese Werte verbessert werden.

TABELLE III.—REPRODUZIERBARKEIT BEIM MESSVORGANG

Element	Ag	Pd	Rh	Au	Pt	Cu	Fe	Ca
Gemessene Linie	$K_{\alpha,Ag}$	$K_{\alpha,Pd}$	$K_{\alpha,Rh}$	$L_{\beta,Au}$	$L_{\beta,Pt}$	$K_{\alpha,Cu}$	$K_{\alpha,Fe}$	$K_{,Ca}$
Mittelwert $\bar{X}$, µg	47,1	44,7	56,4	54,0	68,3	45,4	49,4	48,3
Anzahl n der Messungen	11	11	11	10	11	11	11	11
Variationskoeffizient V, %	4,8	1,5	3,7	4,1	5,5	3,4	3,2	1,0

Es wurde das Verhältnis $I_{K\alpha}/I_{K\alpha(std)}$ bzw. $I_{L\beta}/I_{L\beta(std)}$ für jede Messung berechnet. Die Intensität $I_{K\alpha(std)}$ bezieht sich auf einen äußeren Standard.

Die unter Verwendung des Ringofens erhaltenen Ergebnisse stimmen annähernd mit den von McNevin und Hakkila erhaltenen Werten[7] für die Reproduzierbarkeit

TABELLE IV.—REPRODUZIERBARKEIT BEI DER PROBENVORBEREITUNG

Element	Ag	Pd	Rh	Au	Pt	Cu	Fe	Ca
Meßverfahren	$\frac{I_{\mathrm{Ag-K}\alpha}}{I_{\mathrm{Ag-K}\alpha(\mathrm{std})}}$	$\frac{I_{\mathrm{Pd-K}\alpha}}{I_{\mathrm{U}(15\cdot 00)}}$	$\frac{I_{\mathrm{Rh-K}\alpha}}{I_{\mathrm{U}(19\cdot 00)}}$	$\frac{I_{\mathrm{Au-L}\beta}}{I_{\mathrm{Au-L}\beta(\mathrm{std})}}$	$\frac{I_{\mathrm{Pt-L}\beta}}{I_{\mathrm{Pt-L}\beta(\mathrm{std})}}$	$\frac{I_{\mathrm{Cu-K}\alpha}}{I_{\mathrm{Cu-K}\alpha(\mathrm{std})}}$	$\frac{I_{\mathrm{Fe-K}\alpha}}{I_{\mathrm{Fe-K}\alpha(\mathrm{std})}}$	$\frac{I_{\mathrm{Ca-K}\alpha}}{I_{\mathrm{Ca-K}\alpha(\mathrm{std})}}$
Mittelwert $\bar{X}$, μg	46,1	42,8	55,1	46,5	42,7	46,7	45,4	43,1
Anzahl n der Proben	11	10	11	10	11	11	11	10
Variationskoeffizient V, %	21,5	15,2	6,8	13,2	14,2	9,3	9,3	23,0

Std = äußerer Standard; U = Untergrund.

überein. Die Autoren brachten jeweils 1 ml der zu untersuchenden Lösung auf Filterpapier und dampften die Lösung dann auf einer Heizplatte ein. Auf diesem Wege bestimmten sie 100 μg/ml Palladium, 140 μg/ml Rhodium, 20 μg/ml Iridium und 200 μg/ml Platin, wobei die Variationskoeffizienten zwischen 7 und 13 % lagen. Die Verfasser verwendeten für ihre Untesuchungen teilwise eine Anregungsspannung von 100 kV, wodurch die Empfindlichkeit für Platin and Iridium (Anregung der K-Spektren) erheblich gesteigert und die Reproduzierbarkeit für alle Elemente verbessert werden konnte.

Auswahl der Papiersorte

Die Wahl der Papiersorte wird in erster Linie durch den Einsatz des Ringofens bestimmt. Für das Verfahren eignen sich besonders mittelstarke, gut saugende, säuregewaschene Qualitäten. Um aber den Einfluß der Papiereigenschaft auf die Fluoreszenzstrahlung zu prüfen, ist von einer Reihe säuregewaschener Chromatographiepapiere die Untergrundstrahlung für die Elemente Eisen, Kupfer und Calcium geprüft worden, die von der Herstellung her noch im Papier zu erwarten sind. Die Ergebnisse sind in Tabelle V zusammengestellt.

TABELLE V.—IMPULSVERHÄLTNIS FÜR DIE UNTERGRUNDSTRAHLUNG EINIGER PAPIERSORTEN

Sorte	Flächengewicht, *$\mu g/mm^2$*	Papierstärke, *mm*	Impulsverhältnis Kupfer	 Eisen	 Calcium
FN 15	93	0,18	0,493	0,292	0,435
FN 13	94	0,18	0,950	0,289	0,436
FN 11	98	0,18	0,503	0,294	0,447
FN 12	182	0,20	0,508	0,287	0,326
WF 16	161	0,20	0,496	0,273	0,269
FN 17	160	0,28	0,492	0,271	0,264
FN 18	290	0,51	0,504	0,243	0,165

Bei der Kupfer-Linie ist kein Zusammenhang zwischen Papierstärke und Fluoreszenzstrahlung des Untergrundes feststellbar. Dagegen zeichnet sich aber etwas beim Eisen und deutlich beim Calcium ein Gang ab. Mit zunehmender Papierstärke und damit mit steigendem Flächengewicht nimmt die Blindstrahlung dieser Elemente ab, wobei der Intensitätsrückgang der Ca–K$\alpha_{1,2}$ Linie erwartungsgemäß stärker ausgeprägt ist. Diese Tatsache kann durch zunehmende Absorption der Sekundärstrahlung in der Papierschicht erklärt werden, da die Fluoreszenzstrahlung von Eisen und Calcium schon ziemlich langwellig ist. Aus diesen Untersuchungen resultiert, daß man auch für die röntgenspektrometrische Analyse keine zu dicken Papiersorten verwenden darf.

Zeitlich-ökonomische Betrachtungen

Bei Anwendung der Ringofentechnik benötigt man zum Auftragen von 1 ml einer Lösung etwa 60 min. Da man aber ohne Schwierigkeit—auch ohne Verwendung automatischer Dosiervorrichtungen—fünf Ringöfen gleichzeitig bedienen kann, sinkt die Präparationsdauer auf etwa 12 min pro Probe.

Die Meßzeit beträgt—in Abhängigkeit vom verwendeten Gerät—etwa 10 min für 7 Linien. Einschließlich der Auswertung der ausgedruckten Impulse resultiert daraus eine Gesamtarbeitszeit von 80 min für eine Probe und von 30 min bei gleichzeitigem Einsatz von 5 Ringöfen. Aus dieser Betrachtung geht deutlich hervor, daß das Verhältnis von Dauer der Probenvorbereitung zu Meßzeit noch recht ungünstig ist.

Wachsringtechnik

Abschließend soll deshalb noch kurz auf einige Untersuchungen zur "Wachsringtechnik" nach Johnson und Nagel[8] hingewiesen werden. Man verfährt dabei so, daß man auf einem Blatt eines geeigneten Filtrierpapiers (z.B. FN 12 des VEB Spezialpapierfabrik Niederschlag) die saugfähige Fläche mit Wachs auf einen innerem Durchmesser von 18 mm begrenzt. In das Innere des Kreises gibt man mit Hilfe einer geeigneten Dosierspritze die zu untersuchende Lösung und trocknet an der Luft. Gegenüberder oben beschriebenen Präparationstechnik ist dabei von Nachteil, daß man nur etwa 50 μl auftragen kann. Vorteilhaft ist aber die sehr kurze Auftragezeit von etwa 1,5 min. Der für Cu-$K_{\alpha 1,2}$ ermittelte Variationskoeffizient betrug 8,3%. Für Ag-$k_{\alpha 1,2}$ erhielten wir 11%.

Summary—It has been shown that filter paper is a suitable support material for X-ray fluorescence analysis, but that the use of the Weisz ring-oven enables a higher sensitivity to be obtained with a sufficiently reproducible sample geometry. Linear calibration plots are obtained for Ag, Pd, Rh, Pt, Au, Cu, Fe and Ca in the range 8–100 μg. The relative standard deviations vary between 7 and 35, and the limits of detection range from 8 to 35 μg/ml (for iron and calcium respectively). Five samples may be analysed in 30 min. Use of the wax-ring technique enables the analysis time to be halved, but the sensitivity is then less.

Résumé—On a montré que le papier filtre est une matière support convenable pour l'analyse par fluorescence de rayons X, mais que l'emploi du four annulaire de Weisz permet d'obtenir une sensibilité plus élevée avec une géométrie d'échantillon suffisamment reproductible. On a obtenu des courbes d'étalonnage linéaires pour Ag, Pd, Rh, Pt, Au, Cu, Fe et Ca dans le domaine 8–100 μg. Les écartes types relatifs varient entre 7 et 35, et les limites de détection vont de 8 à 35 μg/ml (pour le fer et le calcium respectivement). On peut analyser cinq échantillons en 30 mn. L'emploi de la technique à l'anneau de cire permet de diviser le temps de l'analyse par deux, mais la sensibilité est alors plus faible.

LITERATUR

1. R.-K. Koch, Diplomarbeit Bergakademie Freiberg, 1968.
2. H. Weisz, *Microanalysis by the Ring Oven Technique*, Pergamon, London, 1961.
3. R. Püschel, *Mikrochim. Acta*, 1965, 770.
4. S. Natelson und B. Sheid, *Anal. Chem.*, 1961, **33**, 396.
5. H. Kaiser, *Z. Anal. Chem.*, 1965, **209**, 1.
6. K. Doerffel, *Statistik in der analytischen Chemie*, VEB Dtsch. Verl. Grundstoffind., Leipzig, 1966.
7. W. M. McNevin und E. A. Hakkila, *Anal. Chem.*, 1957, **29**, 1019.
8. J. L. Johnson und B. E. Nagel, *Mikrochim. Acta*, 1963, 525.

Talanta, 1972, Vol. 19, pp. 299 to 306. Pergamon Press. Printed in Northern Ireland

ELECTROPHORETIC DETERMINATION OF pK-VALUES OF INDICATORS AND THEIR RELATION TO COLOUR CHANGES

I. MORI and M. SHINOGI
Kobe Pharamaceutical Women's College, Nakano 450,
Motoyama-cho, Higashi-Nada-Ku, Kobe, Japan

E. FALK and Y. KISO
Research Reactor Institute, Kyoto University, Kumatori-cho,
Sennan-gun, Osaka-fu, Japan

(*Received* 28 *December* 1970. *Revised* 13 *April* 1971. *Accepted* 3 *August* 1971)

Summary—The pK-values of Xylenol Orange, Pyrocatechol Violet, Thorin and Alizarin Complexone were determined electrophoretically on the basis of the Kiso equation. The colour changes of Xylenol Orange and Alizarin Complexone were found to take place at slightly higher pH values than the electrophoretically determined pK-values. The Kiso-equation for determination of the pK values by electrophoresis yielded reproducible results and the method is useful for complicated substances because the procedure is simple, the equipment inexpensive and only microamounts of the substances are needed.

UNTIL recently paper electrophoresis was applied only to the qualititative separation of various organic and inorganic substances, mainly because of lack of theoretically predictable migration distances. There seemed to be too many variables for a generally applicable theory to be developed. Recently, however, some attempts at a mathematical treatment have been made.[1] A general equation was derived by Kiso *et al.*,[2] calculating the relative electrophoretic mobilities of substances from their molecular weight and pK, and the pH of the background solution. Waldron-Edward had earlier determined the pK-values of a few monobasic amino-acids[3] on the basis of an equation published by Consden, Gordon and Martin.[4] This equation permitted the determination of the pK-values of a monobasic acid, and of both pK-values of a dibasic acid if the difference between them was at least 4 units. The Kiso-equation is applicable to substances with several dissociable protons. The Kiso-equation is:

$$U = \frac{1}{2} \sum_{i=1}^{n} \frac{a}{\sqrt{M}} \left\{1 + \tanh\left[\frac{2.303}{2}(\text{pH} - \text{p}K_i)\right]\right\}$$

where U is the relative mobility of the substance, M the molecular weight, a a constant depending on the substance used as migration standard, and $\text{p}K_i$ the ith dissociation constant of the substance. The migration distance L is directly proportional to U:

$$L = UEt$$

where E is the potential gradient and t the migration time.

From this equation the mobility *vs.* pH or migration distance *vs.* pH curves for various substances can be drawn. From the latter it should be possible to read the pK-values of substances of known molecular weight. This could be confirmed by applying the equation to simple acids such as the various phosphorus acids.[2] We have tried to show that this theory can be applied not only to simple acids but also complex substances such as indicators. The indicators tested were Xylenol Orange, Pyrocatechol Violet, Thorin, Alizarin Complexone, Calcon and Eriochrome Black T.

EXPERIMENTAL

A 10-chamber Toyo Model MC-10K electrophoresis apparatus was used. Cooling water thermostatically controlled at 10° was passed through cooling pipes to keep the coolant, carbon tetrachloride, at constant temperature. Toyo Roshi Paper No. 51A was used in 0·40-m strips as supporting material. The paper was soaked with the buffer solution and a few μl of the indicator solution were applied with a capillary. Picric acid was the migration standard on every strip. Generally 1000 V (Toyo Kagaku Sangyo Model IV power supply) were applied for 60 min. The current was 2–80 mA, depending on the pH of the background buffer solution. The corrected migration distance was derived from the formula

$$L_{\mathrm{corr}} = L_{\mathrm{exp}} \frac{L_{\mathrm{p.t}}}{L_{\mathrm{p.exp}}}$$

where L_{corr} is the corrected migration distance, L_{exp} the experimental migration distance, $L_{\mathrm{p.t}}$ the theoretical migration distance of picric acid (the mean for the particular series of experiments) and $L_{\mathrm{p.exp}}$ the experimental migration distance of picric acid.

The pK of picric acid is 0·38. Between pH 0 and 2 an equilibrium exists between undissociated picric acid and its anion. Only the anion shows the well-known yellow colour which in the electrophoretic experiments was visible only at pH > 1·8. Hence in the pH range 0·5–1·8 no migration standard could be used. The concentration of the solutions was 0·1M. The buffer mixtures used were: pH 0·5–2·0, glycine and hydrochloric acid (0·1M; 2·0–5·4, citric acid and hydrochloric acid or sodium hydroxide; 5·0–7·4, disodium hydrogen phosphate and potassium dihydrogen phosphate; 7·2–9·1, borax and sodium hydroxide; 9·0–12·0, glycine and sodium hydroxide.

RESULTS AND DISCUSSION

Xylenol Orange

The pK values for Xylenol Orange reported by Murakami *et al.*[5] differ slightly from those given by Rehak and Körbl,[6] mainly in the acidic pH range. This was attributed by the former to the use of an impure sample by the latter authors. The values reported by Akhmedli and Imamverdieva[7] were very different.

	Murakami *et al.*[5]	Rehak and Körbl[6]	Akhmedli and Imamverdieva[7]
	(1967)	(1960)	(1966)
pK_1	<1·5	—	—
pK_2	2·32	2·6	—
pK_3	2·85	3·2	4·15
pK_4	6·67	6·4	—
pK_5	10·39	10·5	7·21
pK_6	12·23	12·3	10·72

Our experimentally obtained migration distance *vs.* pH curve is given in Fig. 1. The pH differences for the first three dissociations are only 0·9 and 1·05 pH units, and hence too small to allow separate detection of these steps by electrophoresis. However the increase in the migration distance is about three times that for each of the two further dissociations, indicating a charge increase of three units. According to this assumption the three pK values can be estimated as pK_1 = 1·25, pK_2 = 2·15 and pK_3 = 3·2, which is in agreement with the reported data. These three dissociation steps do not cause any colour change. The solution is yellow and has an absorption maximum at 435 nm. At pH 6·5 another maximum appears at 580 nm, becoming prominent at pH 7·0 and being the only one at pH > 8·0. The colour is then red. The corresponding dissociation equilibrium can be easily detected by electrophoresis, though the value pK_4 = 6·1 determined electrophoretically seems to be too low compared with the optical data and the reported values. The pK_5 determined by electrophoresis is 10·0. This step causes no colour change, and the pK value also seems to be rather low. The pK_6 cannot be determined by electrophoresis. Murakami *et al.*[5] report that the Dotite reagent, which we used for our experiments, contains impurities, but this should not cause shifts of the electrophoretically determined

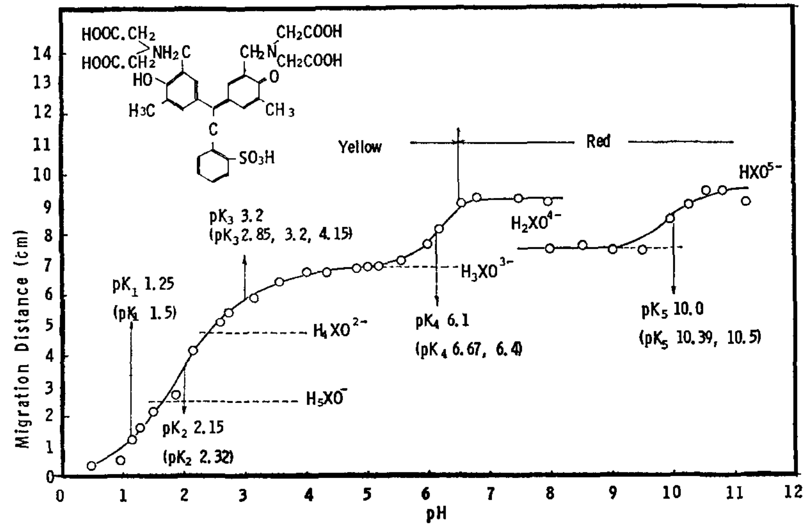


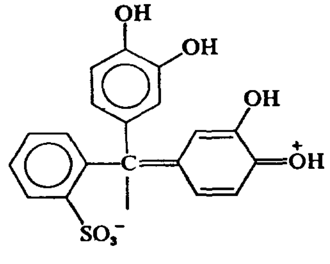
FIG. 1.—Corrected migration distance plotted against pH for Xylenol Orange. pK values are marked and previously published values given in brackets. The colours of the solution are indicated above the curve.

pK-values, as the impurities should have different mobilities and hence be separated from the main compound in our experiment. The reason for the lower values of the electrophoretically determined pK-values has still to be found.

The discontinuity in Fig. 1 and other figures is caused mainly by the change of temperature and ionic strength in the supporting medium. The mobility depends on the ionic strength $I = \frac{1}{2} . c_i z_i^2$, where c_i, the concentration and z_i the charge of the ions. In our experiments the concentration of the buffer solutions was kept constant but the mean charge of the buffer ions varied from buffer solution to buffer solution thus causing differences in the ionic strength and hence in the temperature. We repeated our experiments several times and used chemically different buffer solutions with identical pH values to try to avoid any mistakes. We are further improving the experimental conditions, mainly by keeping constant the ionic strength as well as the concentration of the buffers. If the ionic strength is kept constant the migration distance *vs.* pH curve become a continuous line. It was assumed that when a discontinuity occurred the lower curve could simply be shifted vertically until it became an extension of the upper curve.

Pyrocatechol Violet

The mobility *vs.* pH curve is given in Fig. 2. The reported pK values[8] are also shown. Suk and Malát[9] report the existence of a zwitterion at pH < 1·5:



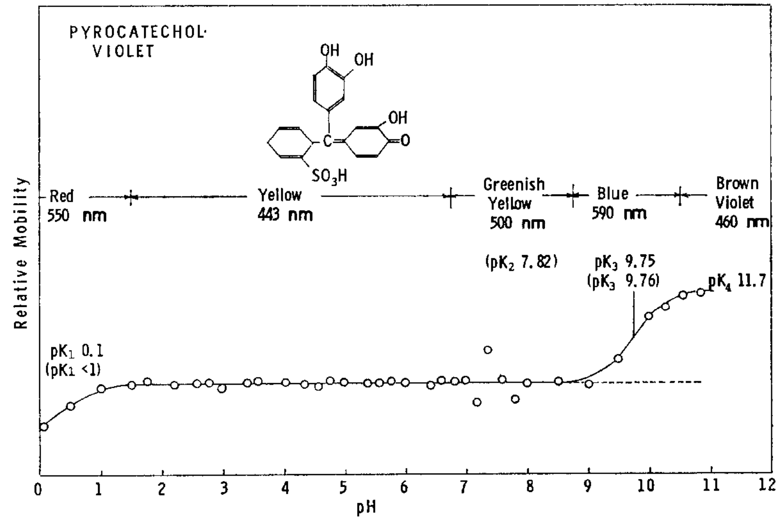


FIG. 2.—Corrected migration distance *vs.* pH for Pyrocatechol Violet. Dotted line; theoretical curve, full line: experimentally obtained.

Electrophoretic evidence for the existence of this species can be found, as the species shows a rather low mobility at pH < 1. Under these conditions the electro-osmotic flow does not lower the migration distance, so all neutral species should have zero mobility. In our experiments the species moved as an anion with low charge. At pH 1·5 the absorption maximum is at 443 nm and the solution is yellow. The zwitterion is reported to be red[10] with an absorption maximum at about 550 nm[9] which can be detected at about pH 0·12, the maximum at 443 nm still being prominent. Only below pH 0 does the maximum at 443 nm completely disappear.

For pH 1·5–7·0 the experimental results are in good agreement with calculation, showing no change in migration distance, and the experimental error is small. The dissociation of the first phenolic hydrogen, with pK = 7·82,[9] cannot be detected by this method. However, at pH = 7·2 the experimental error suddenly increases a great deal. In the absorption spectrum (Fig. 3) a small shoulder with a maximum at 590 nm is found at pH 6·5. Below pH 7·0 the colour appears yellow; at pH 7·0 it is greenish-yellow and besides the maximum at 443 nm a small one is found at 590 nm. At pH 7·5 these maxima are equal in height and the solution is greyish green. At pH 7·7 the 590 nm peak is higher than the one at 443 nm and the colour is grey; at pH 8·0 the solution is red and there is only the maximum at 500 nm. These colours are all stable for 1–2 weeks; after about a month they change slowly. These frequent colour changes and the very poor reproducibility of the electrophoretic results indicate an equilibrium of at least two species with different charges and hence different electrophoretic mobilities. The results also indicate that the transition is not a simple dissociation of a proton as stated by Suk and Malát[9] but a rearrangement within the molecule. The red species obtained at pH 8·0 (λ_{max} 500 nm) is stable up to pH 9·0. At pH 9·3 the solution is deep blue, λ_{max} 590 nm. This blue colour is stable between pH 9·3 and 10·0; at higher pH values the blue colour appears immediately the indicator is added to the buffer but changes within 2 min to violet, there being a broad absorption band with a flat maximum at 460 nm. This is in

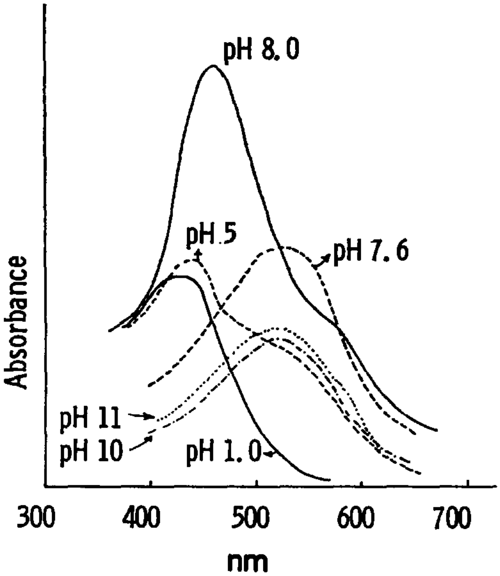


FIG. 3.—Spectra of Pyrocatechol Violet at different pH values (visible region).

agreement with the electrophoretic results, where an increase in migration distance starts at pH 9·0. The electrophoretically determined p*K* of 9·75 is in excellent agreement with the reported value[9] of 9·76. Our investigations did not always confirm the results of Suk and Malát, especially the spectra, and the electrophoretic results in the neutral and alkaline region seemed to show that the dissociation equilibria suggested by them are over-simplified.

Thorin

Thorin has been studied in detail by Margerum *et al.*,[11] who gave the dissociation constants of the two protons of the arsonic group as $pK_3 = 3{\cdot}7$ and $pK_4 = 8{\cdot}3$, and the constant for the naphtholic group as $pK_5 = 11.6$; they could not determine the dissociation constants of the two sulphonic groups. Figure 4, based on the electrophoretic experiments, shows dissociation steps at pK 3·6, 7·4 and 10·2. The migration distance at pH 1 is rather large, suggesting that the migration species has two negative charges; hence the pK values of the two sulphonic groups are less than 0·5. This confirms the assumption of Margerum and his co-workers. The value p*K* 3·6 for dissociation of the first arsonic proton agrees with Margerum's results but pK_4 and pK_5 are lower. The increase in mobility between pH 6 and 9 is rather large, and indicative of a charge increase of two units rather than one. This large increase in migration distance and the discrepancy between Margerum's results and ours will be further studied.

Thorin is red-orange in solution and the absorption maximum at 445 nm is not affected by pH change.

Alizarin Complexone

For Alizarin Complexone we could not find p*K* values in the literature. From our experiments we obtained reproducible values of 3·7, 6·7 and 10·5 (Fig. 5). We ascribe the first two steps to dissociation of the two carboxylic proton and the third to

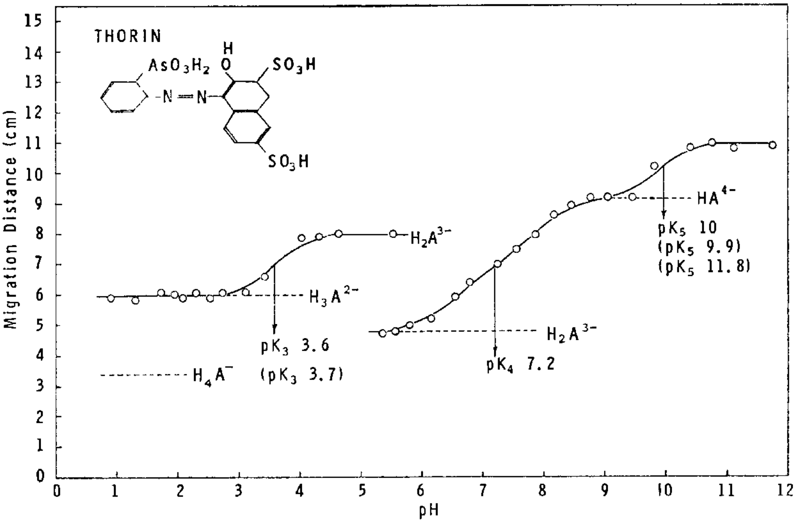


FIG. 4.—Thorin: corrected migration distance *vs*. pH.

dissociation of the first phenolic proton. The solution is yellow below pH 5·0, with an absorption maximum at 425 nm (Fig. 6). At pH 5·0, another maximum appears at 510 nm and is the only one between pH 6·0 and 7·6, the solution being red. Belcher *et al.*[12] reported the colour to be yellow below pH 4·5, red at pH 7–10, mauve at pH 11·5 and violet at pH 12. Unlike these authors we found another colour change from red to yellow at pH 8·0 (absorption maximum 455–460 nm). This yellow colour is stable between pH 8·0 and 9·0. At pH 9·6 it changes back to red (λ_{max} 507 nm), At pH 11 we found a slight shift of the absorption maximum, the peak being rather broad and having a shoulder (the colour being red violet). The colour changes from yellow to red, red to yellow and red to red-violet are all sharp, but the pH values at which they occur are higher than the pK values measured by electrophoresis. The

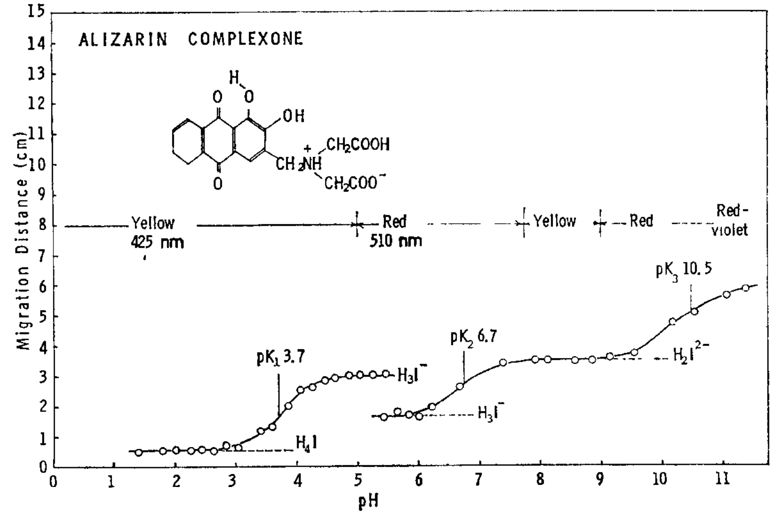


FIG. 5.—Alizarin Complexone: corrected migration distance *vs*. pH.

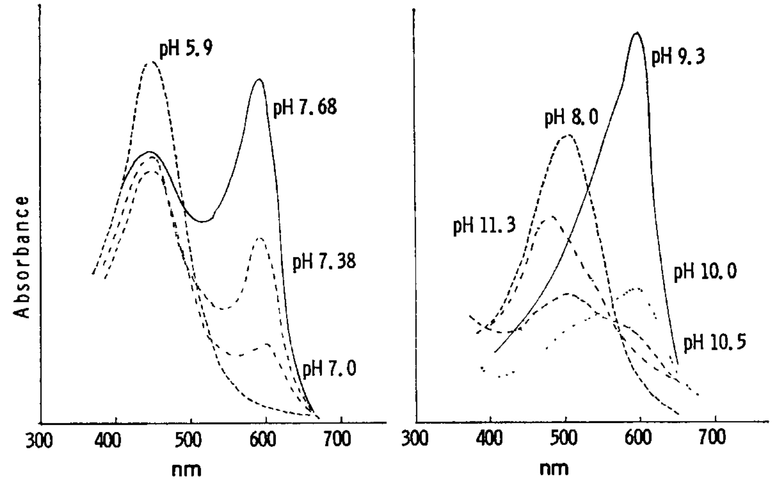


FIG. 6.—Spectra of Alizarin Complexone at different pH values (visible region).

reason seems to be that the colour change can be seen only when the dissociation is nearly complete.

Calcon and Eriochrome Black T

The pK values of these two substances could not be determined by electrophoretic experiments. Each has two naphthyl groups within the molecule, and these cause such strong adsorption on the chromatographic paper that the indicators do not move under our experimental conditions even at the highest pH used.

Zusammenfassung—Die pK-Werte von Xylenolorange, Brenzcatechinviolett, Thorin und Alizarinkomplexon wurden elektrophoretisch auf Grund der Kiso-Gleichung ermittelt. Es wurde gefunden, daß die Farbänderungen von Xylenolorange und Alizarinkomplexon bei geringfügig höheren pH-Werten stattfinden als bei den elektrophoretisch bestimmten pK-Werten. Die Kiso-Gleichung zur Bestimmung von pK-Werten durch Elektrophorese ergab reproduzierbare Ergebnisse. Die Methode ist für komplizierte Substanzen nützlich, da das Verfahren einfach und die Ausrüstung nicht teuer ist und nur Mikromengen Substanz benötigt werden.

Résumé—On a déterminé électrophorétiquement les valeurs de pK des composés Orangé Xylénol, Violet de Pyrocatéchol, Thorin et Alizarine Complexon, sur la base de l'équation de Kiso. On a trouvé que les changements de coloration de l'Orangé Xylénol et de l'Alizarine Complexon se produisent à des valeurs de pH légèrement plus élevées que les valeurs de pK déterminées électrophorétiquement. L'équation de Kiso pour la détermination des valeurs de pK par électrophorèse fournit des résultats reproductibles et la méthode est utile pour les substances compliquées car la technique est simple, l'équipement peu onéreux et des microquantités seulement de substances sont nécessaires.

REFERENCES

1. V. Jokl, *J. Chromatog.*, 1964, **13**, 451.
2. Y. Kiso, M. Kobayashi, Y. Kitaoka, K. Kawamoto and J. Takada, *ibid.*, 1968, **36**, 215.
3. D. Waldron-Edward, *ibid.*, 1965, **20**, 556.
4. R. Consden, A. H. Gordon and A. J. P. Martin, *Biochem. J.*, 1946, **40**, 53.

5. M. Murakami, T. Yoshino and S. Harasawa, *Talanta*, 1968, **14**, 1293.
6. B. Rehak and J. Körbl, *Collection Czech. Chem. Commun.*, 1960, **25**, 797.
7. M. A. Akhmedli and F. B. Imamverdieva, *Azerb. Khim. Zh.*, 1966, 122.
8. O. Ryba, J. Cifka, M. Malát and V. Suk, *Collection Czech. Chem. Commun.*, 1956, **21**, 349.
9. V. Suk and M. Malát, *Chemist-Analyst*, 1956, **45**, 30.
10. W. J. Ross and J. C. White, *Anal. Chem.*, 1961, **33**, 422.
11. D. W. Margerum, C. H. Byrd, S. A. Reed and C. V. Banks, *ibid.*, 1953, **25**, 1219.
12. R. Belcher, M. A. Leonard and T. S. West, *J. Chem. Soc.*, 1958, 2390.

Talanta, 1972, Vol. 19, pp. 307 to 315. Pergamon Press. Printed in Northern Ireland

APPLICATION OF DISPLACEMENT REACTIONS IN FLAME PHOTOMETRY—II

EMISSION FLAME PHOTOMETRIC DETERMINATION OF ALKALINE EARTH METALS IN THE PRESENCE OF INTERFERING ANIONS

P. J. Slevin, E. Györy-Szebényi* and G. Svehla
Department of Chemistry, Queen's University, Belfast, U.K.

(*Received* 15 *July* 1970. *Revised* 30 *September* 1971 *Accepted* 7 *October* 1971)

Summary—For the emission flame photometric determination of strontium and barium in the presence of interfering ions such as phosphate, sulphate, arsenate and oxalate, calibration or simple standard addition methods cannot be used. Greatly reduced errors can be achieved by dividing the sample solution into four equal parts and adding to each certain known amounts of two metal ions. One of these is identical to the determinand (*e.g.*, strontium or barium) the other has similar characteristics to it (*e.g.*, calcium). The amounts of these metals are chosen so that the total (molar) concentration of these should be identical in all solutions, but the ratio of the concentrations of the two metals should be different. The emission of the determinand metal must be measured, and a standard addition plot produced. The amount of determinand present in the sample can be obtained from the intersection of the emission *vs.* concentration line with the concentration axis.

Although the depressive anion interference effects in the flame photometric determination of the alkaline earths have been well documented, they continue to be of interest. Several authors made detailed studies of these in the early 1950's[1–4] with particular reference to the phosphate and sulphate effects. Excellent reviews of the nature of these effects have been made by Fukushima[5] and Herrmann and Alkemade[6] and the depressive effects have been attributed to the formation of compounds with high vaporization temperatures in the evaporating droplets of the aerosol. More recently attempts have been made to establish the exact identity of these involatile compounds[7,8] and the mechanisms by which they are formed.

For the practical analyst, many techniques have been proposed to eliminate such commonly encountered depressive effects as those of phosphate, sulphate, borate, silicate and arsenate on the emission of alkaline earth metals and on that of calcium in particular. The simplest of these methods is the addition of the interferent in excess. This method is based on the well-known fact that the depressing effect of the interferent increases proportionally with the concentration of the latter only up to a certain well-defined value; above this concentration the emission becomes constant. The decrease of the emission signal may be as high as 80%. A similar difficulty arises when the sample is diluted with water. In less concentrated solutions the relative decrease of emission becomes less, but of course the actual signals are weakened. The use of simulated standards is another possibility, but is commendable only if samples of similar composition are analysed in great numbers. Chemical separation methods, based mainly on the removal of interfering ions by ion-exchange is more attractive

---

* On leave from the Department of Applied Chemistry, Technical University, Budapest, Hungary.

than any of these, but it requires time and skill and the efficiency of the separation has to be checked in order to obtain reliable results. The application of a releasing agent (to which our proposed displacement technique is distantly related) is very simple as it requires only the addition of a further reagent to the sample. but it also has its limitations. Quantitative release is not necessarily attained when making up the solution and in accurate work this has to be checked. The use of large excesses of the releasing agent can also have undesirable side-effects.[9]

These interferences are especially marked if the flame temperature is not too high (*e.g.*, in the air–acetylene premixed laminar flame). At higher temperatures, for example with the nitrous oxide–acetylene flame and with measurement of the emission at a sufficient distance above the burner head, errors due to such interferences can be substantially reduced, if not completely eliminated.[10–12] It is relatively simple to remove this remaining marginal interference by any of the techniques mentioned above when hot flames are used; our displacement method works very efficiently under such circumstances. To illustrate the technique, however, we chose a low-temperature flame for several reasons. As the interferences are more marked under such circumstances, the efficiency of the displacement technique can be better judged. Furthermore, though the application of hot flames would certainly ease the difficulties, this cannot be implemented in all cases without altering or replacing existing instruments. Quite a number of commercial flame photometers are based on the application of the premixed acetylene–air flame. These are in routine use and give satisfactory performance if maintained correctly. For the users of such instruments our method may be the simplest and safest.

The proposed technique is based on a shift of the chemical equilibrium by the addition of a third species, keeping, however, the overall concentration ratio of metal to interferent constant. A complete release of the determinand is not necessary and thus errors due to an assumed complete release or to a large excess of releasing agent do not arise. The sensitivity of the method should be at least as good as a normal calibration procedure using a releasing agent, owing to the fact that the displacement is incorporated in a standard addition procedure. Experimentally the technique is very simple, requiring mixtures of the sample solution and solutions which can be prepared and stored in large amounts. The flame photometric readings are made by using a simple air–acetylene flame and all operations require no specially trained personnel.

Principle of the method

The problem facing the analyst when determining alkaline earth metals by flame photometry in the presence of interfering ions can be appreciated from the lowest curve of Fig. 1 where the emission of calcium is plotted as a function of the concentration of phosphate ions present.

This curve was obtained with a Unicam SP 90 spectrophotometer, operated in its emission mode. Solutions were made up from calcium chloride, phosphoric acid and an excess of hydrochloric acid and water so that the calcium concentration in each solution was $0{\cdot}01M$. An acetylene–air flame was used. A similar curve was obtained with a Zeiss (Jena) Model III flame photometer, using an interference filter with a transmission maximum at 630 nm.

The curve indicates clearly the well-known fact that the emission of calcium decreases considerably with increasing phosphate concentration, until the composition corresponding to the formula $Ca_3(PO_4)_2$ is reached; from then onwards the emission

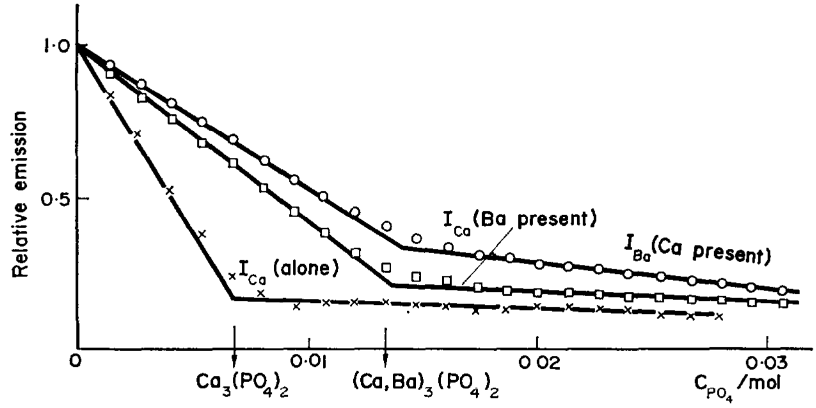


FIG. 1.—Variation of the emission of calcium and barium as a function of the concentration of phosphate.

remains constant. The determination of calcium in the presence of phosphate by making a single emission measurement and using a calibration curve is therefore out of the question. Even the well-known technique of standard addition will not help, because, if calcium ions are added, the relative amounts of calcium and phosphate will change and therefore the degree of interference of phosphate will be different, unless the latter is present in an overwhelming excess.

Such samples can be analysed by using the displacement technique, which is based on the phenomenon that if there are other metal ions present in the sample which will react with the interfering ion in a similar way, a stiuation may arise in which the interferent will react simultaneously with both metals. (An alternative is that the interferent reacts preferentially with one metal; in such a case the displacement technique is not applicable.)

Evidence of such a simultaneous reaction is shown in the upper two curves of Fig. 1. Phosphate was added to mixtures of calcium and barium together with an excess of hydrochloric acid, and the solutions were diluted to a known volume. In each solution the concentrations of calcium and barium ions were 0·01*M*, and the concentrations of phosphate varied between 0 and 0·04*M*. The flame photometric emissions of calcium (at 625 nm) and barium (at 515 nm) were measured separately and the relative emissions plotted as a function of the concentration of phosphate. Both curves show one break-point, corresponding to the formation of a mixed compound, $(Ca,Ba)_3(PO_4)_2$, showing that phosphate was reacting simultaneously with the two metals. (Had phosphate been reacting preferentially with barium, the barium curve would have one break-point where the one was observed with the calcium only, while the calcium curve would have two break-points; first a horizontal line would have been observed up to the break-point of barium, then a decrease would have been observed in the emission up to the second break-point, from which the emission would again have remained constant.)

The displacement technique makes use of the fact that the interfering ion reacts simultaneously with both metals present. This indicates that an equilibrium exists between the determinand *A*, the interfering ion *B* and the displacing agent *M*:

$$AB + M \rightleftharpoons MB + \mathrm{A}$$

where *AB* and *MB* are the refractory compounds which are formed. Such an equilibrium can be shifted in either direction by adding more or less displacing agent to the solution. If we ensure that the ratio of the total concentration of the metal ions and the concentration of the interfering ion is kept constant, we can apply a technique resembling the standard addition method which will provide more reliable results with improved accuracy.

The displacement technique can be applied in the following way. The sample is dissolved and diluted to a known value. Equal aliquots of this stock solution are taken which, (after final dilution) have equal concentrations of the determinand *A* (C_X) and of the interferent *B* (C_B) which are unknown. (All concentrations are expressed in mole/l.) To each of these solutions known amounts of *A* and of the displacing agent *M* are added. The individual amounts must vary, but the addition must be made in such a way that the total concentration of the added ions in the final solutions is equal. Denoting the four aliquots taken from the sample by 1,2,3 and 4, the condition

$$C_{A1} + C_{M1} = C_{A2} + C_{M2} = C_{A3} + C_{M3} = C_{A4} + C_{M4} = \text{constant}$$

must be fulfilled. The purpose of this operation is to keep the ratio $(C_X + C_A + C_M)/C_B$ constant for each aliquot. The flame photometric emission of *A* is then measured. Plotting these emission values as a function of C_A (the known concentrations of the added analyte) gives a straight line which, when extrapolated to the ordinate zero will intersect the abscissa at a point which corresponds to the unknown concentration C_X. These conditions are better seen on the (idealized) diagrams of Fig. 2. The four upper

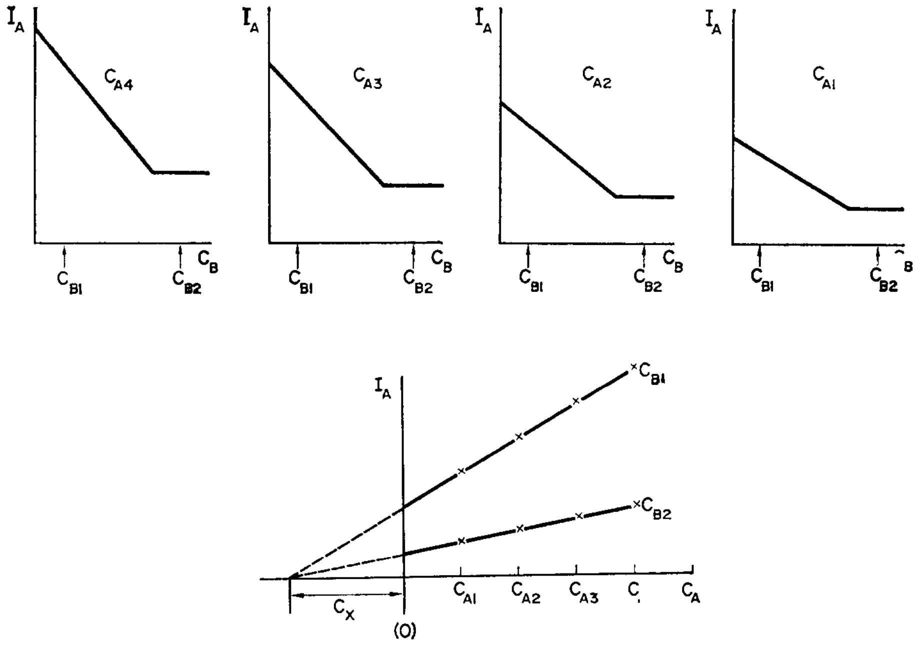


Fig. 2.—Principle of the displacement technique.

curves represent the variation of the emission of the analyte with the concentration of the interfering ions. It is to be noted that if the known concentration C_A is varied, the emission readings will vary proportionally at any fixed concentration C_{B1} or C_{B2} of the interfering ion, but the position of the break-point remains the same because of the presence of the displacing agent. Thus, the emission of the solution at any concentration (C_{B1} or C_{B2}) will be proportional to the total concentration $C_X + C_A$ of the determinand. Thus, intersection of the line with the C_A axis will correspond to the distance of C_X from the origin.

EXPERIMENTAL

Apparatus

A Unicam SP 90 combined emission and atomic-absorption spectrophotometer was used to measure the emission of the solutions. The instrument was equipped with an AEI 10S potentiometer recorder. Readings were made using the standard Méker air–acetylene burner head with the instrument operating in the emission mode. The following parameters were held constant: air flow-rate 5 l./min, burner-height 20 mm (as measured on the scale of the instrument), slit-width 0·1 mm, damping 4. The acetylene flow-rate was adjusted to give the optimum signal in each case, *i.e.*, a maximum signal for a sodium solution at 589 nm. The gain was adjusted as required.

Reagents

Calcium chloride, 0·1*M*. Analytical grade calcium carbonate was dissolved in the minimum amount of dilute hydrochloric acid necessary.

Strontium chloride, 0·1*M*. Prepared from analytical grade strontium chloride hexahydrate by dissolution in water.

Barium chloride, 0·1*M*. Prepared from analytical grade barium chloride dihydrate by dissolution in water.

Lanthanum chloride, 0·1*M*. Prepared by dissolving lanthanum chloride heptahydrate in dilute hydrochloric acid. The lanthanum content was determined by complexometric titration.

Cerium(III) chloride, 0·1*M*. Prepared by dissolving cerous chloride heptahydrate in dilute hydrochloric acid. The cerous content was determined by complexometric titration.

Diammonium hydrogen phosphate, 0·1*M*. Prepared by dissolving the analytical-grade reagent in water.

Sulphuric acid, 0·05*M*. Prepared from concentrated acid by dilution and standardized by acidimetric titration.

Oxalic acid, 0·1*M*. Prepared from analytical grade oxalic acid dihydrate by dissolution in water.

Arsenic acid, 0·1*M*. Prepared from arsenic pentoxide by dissolving in water. The arsenic content estimated by iodimetric titration.

All solutions were made up in demineralized water and stored in polythene containers.

Determination of strontium

Wavelengths. With a monochromator of medium resolution, strontium shows three characteristic emission maxima. The first, at 460·7 nm, is the resonance line of atomic strontium. A strong band system, originating from the emission of SrOH molecules, appears with a maximum at 610 nm, and this peak is closely followed by another, with a maximum at 680 nm. (The latter maximum is the unresolved resultant of four bandheads at 650, 662, 668 and 683 nm respectively.) When the displacement technique is used, the 610-nm band cannot be used because both calcium and lanthanum show a considerable emission in this region. Both the 460·7-nm resonance line and the 690-nm bandhead can be used for the determinations, and it is the characteristics of the photomultiplier which determine the choice between the two wavelengths. In the Unicam SP 90 spectrophotometer the 680-nm bandhead appears to be approximately three times as sensitive as the other, but the precision of the results is equal at both wavelengths.

Choice of the displacing agent. Comprehensive studies were made, using barium, calcium, cerium(III) and lanthanum as displacing agents. Since phosphate showed the most marked interference of those anions examined, the effectiveness of the displacement technique has been checked on solutions containing phosphate alone; the recommended procedures were then applied in the presence of other ions. The displacing agents were introduced as their chlorides, and each solution contained a sufficient (but constant at each concentration range) amount of hydrochloric acid. Three different concentrations 5, 1 and 0·1m*M* strontium, were examined. For each of these concentrations six different molar ratios of phosphate to strontium were investigated, ranging from 0 to 1·25. Four solutions were used in each individual determination, containing $X/2$, X, $3X/2$ and $2X$ amounts of added strontium (where X is the molar concentration of strontium to be determined), and $2X$, $3X/2$, X and $X/2$ amounts of the displacing agent respectively. These values were chosen on the basis of an error calculation, published elsewhere,[18] where it has been shown that for maximum accuracy the ratio of added determinand to unknown should be at least 2. When the solutions were made up, their strontium emission was measured at both the wavelengths mentioned above. Zero emission was adjusted by spraying demineralized water into the flame, as it had been proved that a blank containing $3X$ moles of the displacing agent (plus hydrochloric acid) did not produce any measurable emission at these wavelengths. The solution containing the $2X$ amount of strontium was used to adjust the scale to almost full deflection (about 95%). All the other solutions were then measured and results plotted as shown on the lower curve of Fig. 2. Each determination was repeated three times and the mean result calculated. Results indicated that calcium is the most suitable displacing agent, allowing the determination of strontium with an average error of 5%. For 0·1mM strontium lanthanum(III) is even more suitable, but at higher concentrations lanthanum (and also cerium) gave curved calibration graphs which could not be extrapolated with good accuracy.

In the procedure given below, calcium is therefore recommended as a generally suitable displacing agent. If the results indicate that the unknown concentration of strontium is in the 0·1mM region, a second experiment using lanthanum as a displacing agent might be feasible.

Procedure. Dissolve a sample containing a maximum of 100 mg of strontium and a maximum of 100 mg of phosphate in hydrochloric acid and dilute to 100 ml. Mix, take four 20-ml aliquots in 100-ml volumetric flasks marked A, B, C and D. To A add 10 ml of 0·005M strontium chloride and 40 ml of 0·005M calcium chloride (or less concentrated solutions if the amount of strontium is less). Add 20 + 30 ml for B, 30 + 20 ml for C and 40 + 10 ml for D respectively. Add sufficient hydrochloric acid to each flask to prevent precipitation (using the same amount in each case). Dilute the solutions to the mark and measure the emission of these solutions at 460·7 or 680 nm. Plot the results *vs.* the concentration of added strontium. Draw a straight line through the points and extrapolate until the line intercepts the concentration axis (at "negative" concentration values). The distance from the intercept to the zero point on the concentration axis gives the concentration of the unknown in the final solution.

Results. Results are tabulated in Table I. Note that while the errors obtained by using the standard addition technique alone are as high as ± 20% (depending on the relative concentrations of strontium and the interferent), the displacement method offers much more accurate results. These results also indicate that the determination can be carried out most accurately if the concentration of strontium is kept at the 0·1mM (10 ppm) level and lanthanum is used as a displacing agent.

Determination of barium

Wavelengths. The flame emission spectrum of barium chloride solutions shows the resonance line of barium at 553·6 nm, surrounded by bandheads of BaO emissions. The bandhead at 515 nm is the most sensitive in the air–acetylene flame: it is also a wavelength where there is the least interference from calcium or lanthanum (though the latter shows a considerable background radiation). The 515-nm bandhead was used therefore for the determinations.

Choice of the displacing agent. Calcium, strontium, lanthanum and cerium (III) were used as displacing agents. The pattern of the investigation was similar to that described under strontium. Calcium was again found the most satisfactory displacing agent, but again lanthanum was found to be superior at lower concentrations.

Procedure. Dissolve the sample, containing 0–100 mg of barium and 0–100 mg of the interferent, in hydrochloric acid. Proceed as described for strontium, but use barium chloride solutions instead of strontium chloride and measure the emission at 515 nm. If possible, repeat the experiment at the 0·1mM (10–15 ppm) level with lanthanum as a displacing agent.

Results. Table II shows the results. Sulphate was omitted as an interferent, because at all concentration levels barium sulphate precipitates under these circumstances. Note the advantage of the displacement technique over the simple standard addition method.

Determination of calcium

Experiments on the determination of calcium were made along the lines mentioned above, using strontium, barium, cerium(III) and lanthanum. Of these, strontium seemed to be the best displacing agent, but the errors of the determination were too high (in the 10–20% range) and though these errors were still less than those obtained with the ordinary standard addition technique, the method cannot be recommended for practical analyses. The main difficulty is that because of spectral overlaps, at all feasible wavelengths (the 422·7 nm atomic resonance line and the band heads at around

TABLE I.—DETERMINATION OF STRONTIUM

Concentration of strontium *mM*	Interferent	Concentration of interferent, *mM*	Strontium found, *mM*	Error %
Results of simple standard addition (no displacing agent added)				
0·1	PO_4^{3-}	0·10	0·118	+18
0·1	SO_4^{2-}	0.10	0·117	+17
0·1	AsO_4^{3-}	0·10	0·075	−25
0·1	$(COO)_2^{2-}$	0·10	0·074	−26
Determination of strontium in the presence of phosphate, using calcium as a displacing agent				
5·0	PO_4^{3-}	1·25	5·33	+6·6
5·0	PO_4^{3-}	2·50	5·35	+7·0
5·0	PO_4^{3-}	3·75	5·13	+2·6
5·0	PO_4^{3-}	5·00	5·17	+3·4
5·0	PO_4^{3-}	6·25	5·42	+8·4
1·0	PO_4^{3-}	0·00	1·093	+9·3
1·0	PO_4^{3-}	0·25	1·103	+10·3
1·0	PO_4^{3-}	0·50	1·100	+10·0
1·0	PO_4^{3-}	0·75	1·040	+4·0
1·0	PO_4^{3-}	1·00	1·066	+6·6
1·0	PO_4^{3-}	1·25	1·065	+6·5
0·1	PO_4^{3-}	0·00	0·0953	−4·7
0·1	PO_4^{3-}	0·025	0·0920	−8·0
0·1	PO_4^{3-}	0·050	0·0957	−4·3
0·1	PO_4^{3-}	0·075	0·0970	−3·0
0·1	PO_4^{3-}	0·100	0·103	+3·0
0·1	PO_4^{3-}	0·125	0·102	+2·0
Determination of strontium in the presence of phosphate, using lanthanum as a displacing agent				
0·1	PO_4^{3-}	0·000	0·099	−1·0
0·1	PO_4^{3-}	0·025	0·100	0
0·1	PO_4^{3-}	0·050	0·100	0
0·1	PO_4^{3-}	0·075	0·098	−2·0
0·1	PO_4^{3-}	0·100	0·100	0
0·1	PO_4^{3-}	0·125	0·099	−1·0
Determination of strontium in the presence of various interferents, using lanthanum as displacing agent				
0·1	SO_4^{2-}	0·05	0·102	+2
0·1	SO_4^{2-}	0·10	0·102	+2
0·1	AsO_4^{3-}	0·05	0·100	0
0·1	AsO_4^{3-}	0·10	0·102	+2
0·1	$(COO)_2^{2-}$	0·05	0·100	0
0·1	$(COO)_2^{2-}$	0·10	0·099	−1

550 and 625 nm) there is a measurable contribution of the displacing agent in almost all combinations. The possibility of improving the results by the use of a better monochromator cannot be ruled out, provided that width of emission lines or bands can be decreased considerably.

A method has been worked out —a method based on a different type of displacement reaction—for the determination of calcium. This method is based on the addition of an excess of sulphate to the solution, whereupon all the calcium present is transformed into calcium sulphate. When the solutions are sprayed into an acetylene–air flame, well-defined emissions are obtainable, which with the

TABLE II.—DETERMINATION OF BARIUM

Concentration of barium *mM*	Interferent	Concentration of interferent *mM*	Barium found, *mM*	Error, %
Results of simple standard addition (no displacing agent added)				
0·1	PO_4^{3-}	0·1	0·089	−11
0·1	AsO_4^{3-}	0·1	0·080	−20
0·1	$(COO)_2^{2-}$	0·1	0·077	−23
Determination of barium in the presence of phosphate, using calcium as a displacing agent				
5·0	PO_4^{3-}	0·00	5·166	+3·3
5·0	PO_4^{3-}	1·25	5·460	+9·2
5·0	PO_4^{3-}	2·50	5·616	+12·3
5·0	PO_4^{3-}	3·75	5·616	+12·3
5·0	PO_4^{3-}	5·00	5·883	+17·7
5·0	PO_4^{3-}	6·25	6·066	+21·3
1·0	PO_4^{3-}	0·00	1·000	0
1·0	PO_4^{3-}	0·25	1·066	+6·6
1·0	PO_4^{3-}	0·50	1·092	+9·2
1·0	PO_4^{3-}	0.75	1·123	+12·3
1·0	PO_4^{3-}	1·00	1·076	+7·6
1·0	PO_4^{3-}	1·25	1·130	+13·0
0·1	PO_4^{3-}	0·000	0·0933	−6·7
0·1	PO_4^{3-}	0·025	0·0973	−2·7
0·1	PO_4^{3-}	0·050	0·0953	−4·7
0·1	PO_4^{3-}	0·075	0·1043	+4·3
0·1	PO_4^{3-}	0·100	0·0993	−0·7
0·1	PO_4^{3-}	0·125	0·1044	+4·4
Determination of barium in the presence of phosphate, using lanthanum as a displacing agent				
0·1	PO_4^{3-}	0·000	0·097	−3·0
0·1	PO_4^{3-}	0·025	0·097	−3·0
0·1	PO_4^{3-}	0·050	0·095	−5·0
0·1	PO_4^{3-}	0·075	0·103	+3·0
0·1	PO_4^{3-}	0·100	0·104	+4·0
0·1	PO_4^{3-}	0·125	0·100	0
Determination of barium in the presence of various interferents, using lanthanum as a displacing agent				
0·1	AsO_4^{3-}	0·05	0·096	−4·0
0·1	AsO AsO_4^{3-}	0·10	0·097	−3·0
0·1	$(COO)_2^{2-}$	0·05	0·095	−5·0
0·1	$(COO)_2^{2-}$	0·10	0·094	−6·0

aid of a suitable calibration curve permit the determination of calcium in the presence of phosphate, arsenate and oxalate with an error less than 3–5%. Details of the method have been published elsewhere.[14]

Acknowledgments—The authors wish to thank Professor Cecil L. Wilson for encouragement of this work and the Government of Northern Ireland for a research grant to P. J. S.

Zusammenfassung—Bei der emissionsphotometrischen Bestimmung von Strontium und Barium in Gegenwart störender Ionen wie Phosphat, Sulfat, Arsenat und Oxalat können Eichverfahren oder ein einfaches Zumischverfahren nicht angewandt werden. Man erreicht eine starke Verminderung der Fehler, wenn man die Probenlösung in vier gleiche Teile teilt und jedem bekannte Mengen zweier Metallionen zusetzt. Eines davon ist identisch mit dem zu bestimmenden Ion (z.B. Strontium oder Barium), das andere hat ähnliche Eigenschaften (z.B. Calcium). Die Mengen dieser Metalle werden so gewählt, daß die (molare) Gesamtkonzentration in allen Lösungen gleich, jedoch das Verhältnis der beiden Metalle verschieden ist. Die Emission des zu bestimmenden Metalls wird gemessen und eine Standardzugabekurve aufgezeichnet. Die Menge des in der Lösung anwesenden zu bestimmenden Metalls erhält man aus dem Schnittpunkt der Emissions-Konzentrations-Kurve mit der Konzentrationsachse.

Résumé—On ne peut utiliser les méthodes d'étalonnage ou d'addition d'étalon simples pour le dosage photométrique par émission du strontium et du baryum en la présence d'ions gênants tels que phosphate, sulfate, arséniate et oxalate. On peut obtenir des erreurs fortement réduites en divisant la solution échantillon en quatre parts égales et en ajoutant à chacune certaines quantités connues de deux ions métalliques. L'un de ceux-ci est identique à celui que l'on détermine (par exemple strontium ou baryum), l'autre à des caractéristiques qui lui sont similaires (par exemple calcium). Les quantités de ces métaux sont choisies de sorte que leur concentration totale (molaire) soit identique dans toutes les solutions, mais le rapport des concentrations des deux métaux doit être différent. L'émission du métal que l'on dose doit être mesurée, et l'on doit établir un graphique d'addition type. La quantité de produit à doser présente dans l'échantillon peut être obtenue à partir de l'intersection du tracé de l'émission en fonction de la concentration avec l'axe des concentrations.

REFERENCES

1. G. L. Baker and L. M. Johnson, *Anal. Chem.*, 1954, **26**, 465.
2. A. Strasheim and J. P. Nell, *J. S. African Chem. Inst. N.S.*, 1954, **7**, 79.
3. L. Leyton, *Analyst*, 1954, **79**, 497.
4. P. G. de Montgarevil, *Ph.D. Thesis*, University of Paris, 1954.
5. S. Fukushima, *Mikrochim. Acta*, 1959, 596.
6. R. Herrmann and C. Th. J. Alkemade, *Chemical Analysis by Flame Photometry*, 2nd Ed., Wiley, New York, 1963.
7. I. Rubeska and B. Moldan, *Anal. Chim. Acta*, 1967, **37**, 421.
8. J. Spitz, G. Uny, M. Roux and J. Besson, *Spectrochim. Acta*, 1969, **24B**, 339.
9. V. A. Fassel and D. A. Becker, *Anal. Chem.*, 1969, **41**, 1522.
10. S. R. Koirtyohann and E. E. Pickett, *Spectrochim. Acta*, 1968, **23B**, 673.
11. U. G. Mossotti and M. Duggan, *Appl. Opt.*, 1968, **7**, 1325.
12. E. E. Pickett and S. R. Koirtyohann, *Anal. Chem.*, 1969, **41**, 28A.
13. P. J. Slevin and G. Svehla, *Z. Anal. Chem.*, 1969, **246**, 5.
14. *Idem*, *ibid.*, 1971, **254**, 107.

Talanta, 1972, Vol. 19, pp. 317 to 327. Pergamon Press. Printed in Northern Ireland

A FULLY AUTOMATED PROCEDURE FOR THE DETERMINATION OF SODIUM HYPOCHLORITE AND HYDROGEN PEROXIDE, BASED ON THE USE OF A POROUS CATALYTIC SILVER ELECTRODE

B. FLEET and A. Y. W. HO
Department of Chemistry, Imperial College of Science and Technology,
London, S.W.7, U.K.

J. TENYGL
Polarography Institute, Czechoslovak Academy of Sciences,
Prague, 1, Czechoslovakia

Summary—A new approach to the automated determination of sodium hypochlorite and hydrogen peroxide is described, based on the use of a porous catalytic silver electrode. The principle of both methods involves the quantitative liberation of oxygen, which is measured coulometrically by the electrode. The procedures are suitable for the continuous monitoring of the contents of bleaching baths.

AN EFFICIENT bleaching process must impart to textile goods a pure and permanent white and level-dyeing properties without "tendering" or diminishing the tensile strength. Much of the early work on bleaching processes suffered from lack of sufficiently accurate methods of testing both the bleaching solution and the bleached product. Satisfactory chemical methods of estimating damage of textile material resulting from an inefficiently controlled bleaching process have now been definitely established and have been incorporated in a number of standard methods.[1–4] These include the copper number determination,[1,5] the fluidity test and the solubility test.[4,6] In order to obtain high-quality bleached textile goods which satisfy the relevant specifications, constant surveillance and control at each step of the bleaching process are required.

The two bleaching agents most commonly employed in the textile industry are sodium hypochlorite and hydrogen peroxide, both of which are useful for bleaching cotton, rayon, linen and other cellulosic fibres. Hypochlorite bleach has the advantage of having a long history and hence a well-developed methodology. It is also relatively cheap and capable of giving good results provided that the process has been closely controlled. Hydrogen peroxide has the advantage of being able to deal with unscoured or partially scoured cotton, thus requiring less manipulation of fabric. Another advantage is that it has a much lower degrading action on cellulose and can also be used for bleaching wool, silk and other animal fibres. A comprehensive account of the bleaching procedures based on these bleaching agents has been given by Marsh[7] and Trotman.[8] In general, the most important factors in both bleaching processes are pH, temperature and concentration of the bleaching agent. The first two factors can be readily controlled by using suitable buffers and a thermostatic bleaching bath respectively. In the past, concentration of the bleaching solution has been monitored by conventional titrimetric analyses of grab samples, with obvious shortcomings in time, economy and human error. Adelman[9] has described an automated method for hypochlorite determination, based on measuring the absorbance of the iodine formed by the reaction between hypochlorite and potassium iodide in an acetic acid medium. Automated analysis on a continuous basis offers not only increases in economy, speed and precision but also offers possibilities of continuous monitoring in a process stream. Furthermore, the continuous analytical system can be incorporated into an automated control system in which the controller compares the signal from the sensor with a set signal—any deviation would bring about a corrective action (in this case) by controlling the addition of a concentrated bleach solution from a reservoir. As a result, the concentration of the bleaching bath is maintained at a constant predetermined level.

Although AutoAnalyser systems involving colour development have been very popular, there is no reason to believe that the spectrophotometer is superior to other sensor systems in continuous analysis. Tenygl *et al.*[10] have recently described automated methods for determining dichromate and permanganate, based on the reaction with hydrogen peroxide to liberate oxygen which, in turn, is measured by a new type of coulometric oxygen analyser.[11] An extension of these two methods was found to be satisfactory for the automated determination of dichromate (C.O.D.) and permanganate value of sewage and effluents[12] and also for oxygen determination in clinical analysis.[13] The analytical system involved in all these procedures consisted basically of an oxygen sensor and the Technicon AutoAnalyser. Such a system is highly versatile and can be used to monitor any reaction which is well-defined, reasonably rapid, stoichiometric and does not involve the formation of a precipitate, provided that oxygen is either liberated or consumed. The reactions between hydrogen peroxide and permanganate (or dichromate) and between oxyhaemoglobin and ferricyanide are thus important but not exclusive examples of a large class of reactions which can be monitored by this relatively simple analytical system.

In this study, automated methods for determining hypochlorite and hydrogen peroxide are described. The first is based on the reaction between hypochlorite and hydrogen peroxide in an alkaline medium to liberate oxygen, which is monitored by the coulometric oxygen analyser. With the hydrogen peroxide method, there should theoretically be a wide range of choice of reagent as hydrogen peroxide reacts with several substances, some in acidic medium, others in alkaline medium, to liberate oxygen. Reactions in acid media, however, are not suitable for the present procedure, as the hydrogen peroxide bleach is normally buffered with bicarbonate and the large quantities of carbon dioxide liberated by dilute acids would damage the silver working electrode. Reagents which react with hydrogen peroxide in alkaline medium to liberate oxygen include hypochlorite and periodate. Potassium periodate is used in the present procedure since it is more stable than hypochlorite.

The automated hypochlorite method, as described here, is useful in the textile industry since it permits efficient control of the contents of the hypochlorite bath. This is especially important in bleaching viscose rayon and other regenerated cellulosic fibres since they are more prone to damage than the native cellulosic fibres such as cotton.[7] Although there is less information correlating chemical damage with excess of hydrogen peroxide bleach, the automated hydrogen peroxide method is useful since the reagent is relatively expensive and hence correct control of the bleach bath concentration can lead to appreciable economy by using not more than the required amount of bleach.

EXPERIMENTAL

Apparatus

AutoAnalyser modules (Technicon Corp., Tarrytown, N.Y.) consisting primarily of a sampler and a proportioning pump with associated pump tubes and glass fittings, were used. For procedures in which the integrated current response was used, samples were presented at the rate of 20/hr at a ratio of sample to water wash of 1:2. When the non-integrated current response was used as analytical signal, a sampling rate of 10/hr was used at a ratio of sample to water wash of 1:1.

The oxygen analyser. A detailed description of the construction of the oxygen analyser has already been reported.[11] Basically, it consists of a three-electrode cell (Fig. 1) consisting of a porous catalytic silver electrode (Fig. 2) which is immersed in a 25% potassium hydroxide solution and maintained at −0·85 V *vs.* an Hg/HgO reference electrode by means of a potentiostat; a schematic circuit for this is shown in Fig. 3. The third counter electrode is a platinum wire isolated from the rest of the solution by a glass tube with a sintered-glass base. The gaseous sample stream is analysed by passing through an inlet-outlet manifold into the annular space within the silver working electrodes, where the oxygen is reduced. The electrode reactions involved are:

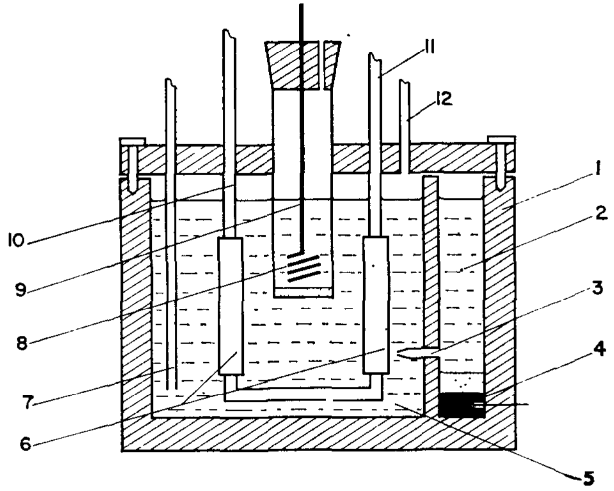


FIG. 1.—The 3-electrode polarographic cell.

(1) Perspex body
(2) 25% potassium hydroxide solution
(3) Capillary probe
(4) Hg/HgO reference electrode
(5) 25% potassium hydroxide solution
(6) Porous silver working electrodes (connected in series)
(7) Inlet tube for degassing
(8) Platinum counter-electrode
(9) 25% potassium hydroxide solution
(10) Sample outlet tube (nickel)
(11) Sample inlet tube (nickel)
(12) Outlet tube for degassing

$$\text{at Ag working electrode: } O_2 + 2H_2O + 4e = 4OH^-$$
$$\text{at Pt counter-electrode: } 4OH^- = O_2 + 2H_2O + 4e$$

The pressure regulator. Efficient working of the porous silver electrodes requires that equilibrium be maintained between the gas and electrolyte-filled pores. This is achieved with the aid of a gas over-pressure against the capillary pressure of the electrode. For the Type LD848 electrodes (Heyrovský Inst. of Polarography, Prague) used in the present study, the hydrodynamic resistance is 10–15 mm Hg and the gas over-pressure used must be greater than this value. There are two simple ways by which a constant gas over-pressure within the electrodes can be maintained. One method depends on differential pumping, with the total (pre-sensor + post-sensor) waste-lines pumping at a rate slower than that of the total feed-in lines. Another method is to place a pressure control valve in line behind the sensor. In the latter method, the flow-rate of the post-sensor waste line is automatically regulated and the gas over-pressure within the electrodes remains constant even when the flow-rates of the feed-in lines are changed. Another advantage is that problems due to pump overloading and pump pulses are much

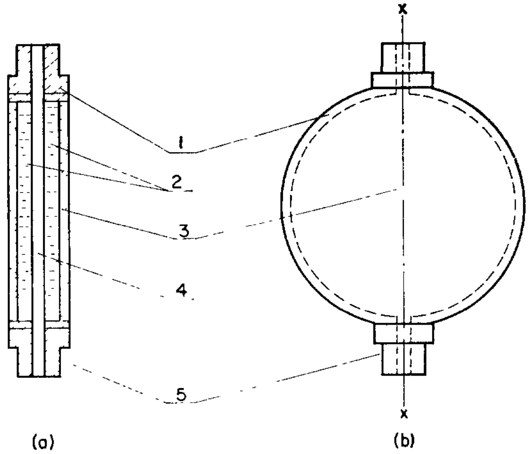


FIG. 2.—The porous silver electrode: (*a*) cross-sectional view X-X; (*b*) external planar view.

(1) Nickel frame
(2) Catalytic operating layers
(3) Protective layers
(4) Annular space
(5) Gas inlet and outlet tubes

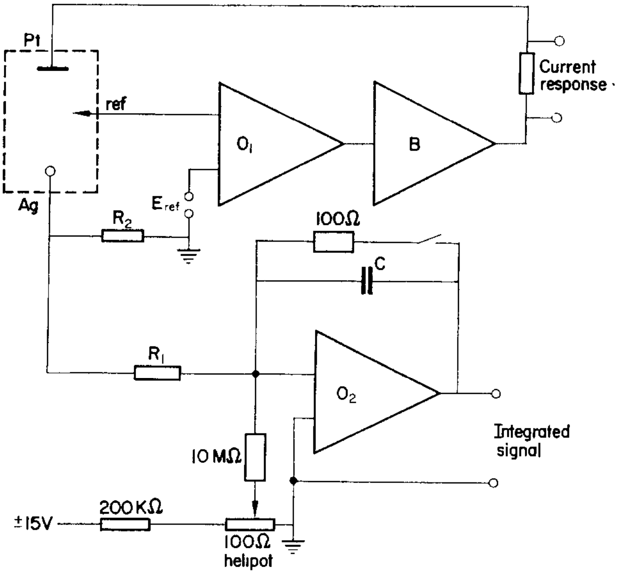


FIG. 3.—A schematic circuit diagram of the potentiostat.

O_1—PF85 Philbrick operational amplifier	R_1 = 30 kΩ
B —Philbrick booster amplifier.	R_2 = 0·5 Ω
O_2—Analog Devices operational amplifier 146J.	C = 0·47μF (polycarbonate)

reduced because the use of the pressure regulator dispenses with the need to pass the post-sensor waste lines through the pump.

Flow diagram

The flow chart for the automated hypochlorite and hydrogen peroxide methods is shown in Fig. 4. Sample (hypochlorite or hydrogen peroxide), reagent (hydrogen peroxide or potassium periodate) and nitrogen are mixed; the oxygen liberated in the reaction is then carried along in the nitrogen stream and presented to the sensor after the liquid phase has been removed by passing the gas-liquid mixture through two consecutive phase separators. A sample-pump tube of very small bore is used for the hydrogen peroxide method because of the relatively high "available" oxygen content of the sample. Manifolds in which only part of a prediluted sample is presented, thus permitting larger initial volume intake of sample, have been tried but were found to be less satisfactory since carry-over tends to increase with increasing complexity of the manifold.

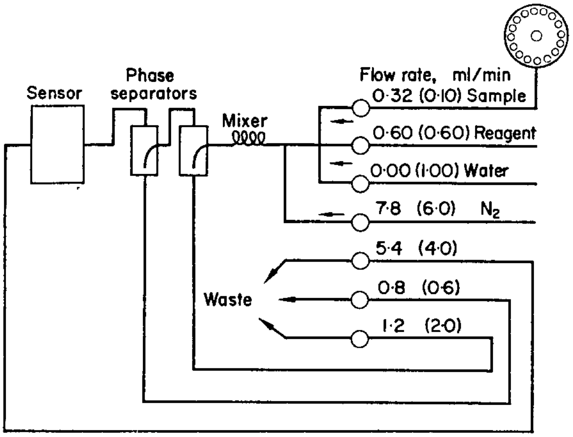


FIG. 4.—Flow diagram for the automated hypochlorite method and hydrogen peroxide method. Tube dimensions in brackets refer to the hydrogen peroxide procedure.

Reagents

All chemicals used were of analytical grade.

Sodium hypochlorite stock solution (~2 *g of Cl/l.*). A strong concentrated sodium hypochlorite solution was diluted with the appropriate amount of distilled water, and 5 g of sodium carbonate were added to make the pH approximately 11. The solution was then standardized against arsenious acid, with Bordeaux as indicator.

Hydrogen peroxide solution (*for the hypochlorite method*). Ten ml of 100-volume hydrogen peroxide were diluted to 1 litre with distilled water. The solution was stored in the dark in a dark glass bottle.

Stock hydrogen peroxide bleach solution (*2-volume standard*). Hydrogen peroxide (100-vol, 20 ml) was added to a solution containing 7 g of sodium silicate (78° Tw), 0·5 g of sodium hydroxide and 1·75 g of sodium carbonate. The solution was diluted to 1 litre with distilled water and standardized iodometrically, with molybdate catalyst, the iodine being titrated in an atmosphere of carbon dioxide or nitrogen. The stock solution was adjusted to exactly 2-volume strength.

Diluent for hydrogen peroxide bleach standards. Prepared by dissolving 7 g of sodium silicate (78° Tw), 1·75 g of sodium carbonate and 0·5 g of sodium hydroxide and diluting to 1 litre with distilled water.

Potassium periodate solution. Potassium periodate (2·3 g) was dissolved in 10 ml of 20% potassium hydroxide solution and the solution made up to 100 ml.

RESULTS AND DISCUSSION

Theory

Sodium hypochlorite reacts with hydrogen peroxide in an alkaline medium to liberate oxygen.

$$NaOCl + H_2O_2 = NaCl + H_2O + O_2$$

Assuming hydrolysis of sodium hypochlorite, this can be written as:

$$OH^- + HOCl + H_2O_2 = Cl^- + 2H_2O + O_2$$

Potassium periodate reacts with hydrogen peroxide in an alkaline medium according to the equation:

$$KIO_4 + H_2O_2 = KIO_3 + H_2O + O_2$$

Assuming hydrolysis of potassium periodate, this can be written as:

$$OH^- + HIO_4 + H_2O_2 = IO_3^- + H_2O + O_2$$

The concentration of available chlorine required in the hypochlorite bleach liquor varies between 1 and 3 g of Cl/l., depending on the type of yarn and the amount of impurities present. The bleach liquor is normally buffered between pH 10 and 11 by the addition of 5 g of sodium carbonate per l. because the active bleaching component varies with the pH of the bath. At pH 10–11, the active component is sodium hypochlorite, but as the pH decreases to 5–8·5, the solution would consist predominantly of free hypochlorous acid, and on further lowering of the pH to below 3, free chlorine would be evolved.[13] The last two situations are undesirable because free hypochlorous acid causes a rapid oxidation and degradation of cellulose and hence excessive damage to the textile material being bleached. In the present study, hypochlorite standards were prepared simulating bleach liquors both in concentration and in pH.

In the case of hydrogen peroxide bleach, the most important factor is to achieve the right degree of stability so that sufficient oxidizing (bleaching) power is attained without danger of rapid exhaustion of hydrogen perioxide through decomposition. The liquor is normally buffered between pH 8 and 10·9 with a mixture of sodium carbonate and sodium hydroxide. Sodium silicate is added as a stabilizer. The basic formula for making up a 1-volume bleach liquor is: water 98 gallons (98 litres); sodium silicate 78° Tw 7 lb (0·7 kg); caustic soda ½ lb (0·05 kg); soda ash 1¾ lb (0·175 kg) and hydrogen peroxide "100 volume" solution, 1 gallon (1·0 litre).[15] Many variations of this basic formula can be used according to the nature of the material, the degree of whiteness called for and the construction of the plant. In this study, however, hydrogen peroxide bleach standards of different strengths were prepared according to the formula above, only the amount of hydrogen peroxide being varied.

Hypochlorite method

Integrated response. The integrated current obtained from hypochlorite standards is summarized in Table I. Samples contained 20·0, 40·0, 60·0, 80·0 and 100·0 ml of stock hypochlorite solution, made up to 100 ml with distilled water. These concentration standards then covered the range from 0·44 to 2·22 g of Cl/l., which is the range normally found in bleach baths. A linear relationship between the integrated response and concentration over the range studied is obtained. The integrated signals obtained for replicate analyses of a series of standards were evaluated statistically (Table I). The reproducibility of the method was found to be satisfactory, with standard deviation 0·40 and coefficient of variation 1·1%.

TABLE I.—INTEGRATED CURRENT SIGNALS AT VARYING CONCENTRATIONS OF HYPOCHLORITE. A STATISTICAL EVALUATION OF THE RESULTS OBTAINED

Sample	Conc. of sample *g of Cl/l.*	Integrated signals (results of replicate analyses) *Recorder units*	Mean	Sum of* squares	Degrees of freedom	Variance
A	0·44	15·5, 16·2, 15·6, 15·5	15·7	0·34	3	0·11
B	0·89	26·5, 27·0, 27·0, 27·5	27·0	0·50	3	0·17
C	1·33	37·5, 37·5, 38·0, 38·5	37·9	0·69	3	0·23
D	1·78	48·2, 48·5, 49·0, 48·0	48·4	0·57	3	0·19
E	2·22	60·0, 60·0,	60·0	0·00	1	0·00
Total			35·33†	2·10	13	0·16‡

Standard deviation, s = 0·40; coefficient of variation, = 1·1%

* Sum of squares $= \sum_{i=1}^{n} (x_i - \bar{x})^2 \doteq \sum_{i=1}^{n} x_i^2 - \left[\sum_{i=1}^{n} x_i\right]^2 / n$

† Weighted mean: ‡ Total of sum of squares/total of degree of freedom.

Non-integrated response. The non-integrated response obtained with hypochlorite standards is summarized in Table II. The same samples were used as for the integrated method. A rectilinear relationship between signal and concentration is again obtained. The reproducibility of the method was found to be slightly better than that of the integrated method, with standard deviation 0·27 and coefficient of variation 0·8% (Table II).

Discrete sample analysis vs. *continuous monitoring.* In analysis of discrete samples with the present apparatus, the integrated method is the obvious choice since the number of samples which can be handled (20/hr) is twice that of the non-integrated method. Because of the simplicity of the manifold, the current-time profile is well-defined and regular. Hence, there should be no problem in linking the integrator to a "super-timer" which governs both the sampling probe and the integrator. In the case of continuous monitoring, however, it is preferable to use the non-integrated method, which is simpler and at the same time exercises a minute-to-minute close control of the process stream. A semi-continuous method may also be useful at times when a less rigorous albeit continuous control of the process stream is desired and this will be discussed below in the hydrogen peroxide method.

TABLE II.—NON-INTEGRATED RESPONSE AT VARYING CONCENTRATIONS OF HYPOCHLORITE. A STATISTICAL EVALUATION OF THE RESULTS OBTAINED

Sample	Conc. of sample *g of Cl/l.*	Non-integrated response (results of replicate analyses) *Recorder units*	Mean	Sum of squares	Degree of freedom	Variance
A	0·44	13·1, 13·2, 13·5, 13·3	13·4	0·15	3	0·050
B	0·89	24·5, 24·5, 24·8, 24·8	24·7	0·10	3	0·033
C	1·33	36·0, 36·0, 36·7, 36·5	36·3	0·26	3	0·087
D	1·78	47·2, 47·5, 48·0, 48·0	47·7	0·47	3	0·157
E	2·22	59·0, 59·0,	59·0	0	1	0·000
Total			33·10	0·98	13	0·075

Standard deviation, 0·27; coefficient of variation, = 0·8%

Dynamic response of the system. The total time-lag between the introduction of sample and the sensor read-out can be divided into two components—the dead-time of the system, which is the time required for the processing of the sample before measurement, and the transition time of the sensor, which is the time required for the sensor to change from the steady state for one sample to that for the next. In analysis of discrete samples, it is the latter factor which controls the sampling rate and hence in such systems efforts have been made to minimize sensor hold-up and hence reduce the transition time. In the case of continuous monitoring, the dead-time is just as important as the sensor transition time because the total response time must be small if close control of the process stream is to be achieved. The dynamic response of the present analytical system as a whole is assessed by stepwise changes (at 5-min intervals) in the concentration of the sample solution which is continuously fed in. Figure 5 shows a recording of the current-time response for five such steps. The dead-time of the system was found to be 2½ mins. The sensor transition (95%) time was about 2 min for a change in concentration Δ[NaOCl] = 0·444 g of Cl/l. This means that any variation in the concentration of the bleach bath can be detected within 2½ mins whereas the full impact of the variation would be felt within another 2 min. Further improvements towards a faster dynamic response of the present system can be achieved by using better manifold designs to minimize hold-up in the processing units and flow-system preceding the sensor. It may also be possible to reduce the transition time by using flow-through sensor electrodes of smaller capacity. For most practical purposes, however, the dynamic response of the present system should be good enough for bleach liquor control.

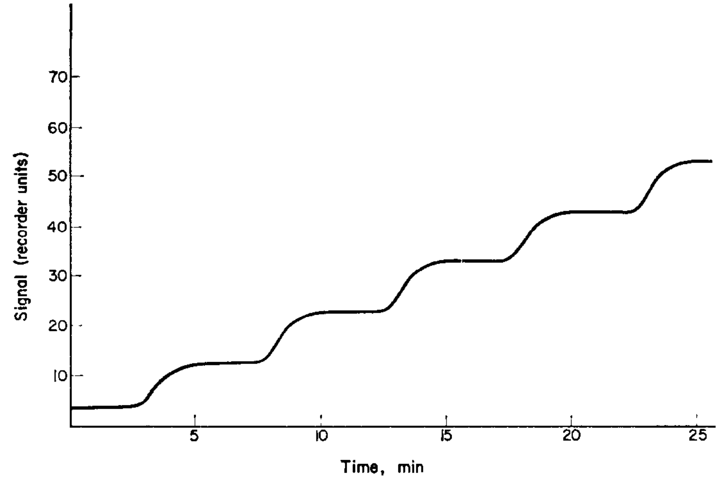


Fig. 5.—Current-time waves obtained with stepwise increase in concentration of the hypochlorite sample at 5-minute intervals.

Hydrogen peroxide method

Integrated response. The integrated current response obtained with hydrogen peroxide bleach standards is shown in Table III. Samples contained 10·0, 20·0, 30·0, 40·0, 50·0 and 60·0 ml of the stock 2-volume standard, made up to 100 ml with the diluent solution. These concentration standards then covered the range of 0·2–1·2 volume hydrogen peroxide. A rectilinear relationship between the integrated signal and concentration over the range studied is obtained. The reproducibility of the

Table III.—Integrated current signals at varying concentrations of hydrogen peroxide. A statistical evaluation of the results obtained

Sample	Conc. of sample *Volume* H_2O_2	Integrated signal (results of replicate analyses) *Recorder units*	Mean	Sum of squares	Degrees of freedom	Variance
A	0·2	16·2, 16·8, 16·5, 16·5	16·5	0·18	3	0·06
B	0·4	28·4, 29·4, 29·3, 28·9	29·0	0·62	3	0·21
C	0·6	41·5, 43·4, 34·1, 42·0	42·5	2·42	3	0·81
D	0·8	55·5, 56·4, 54·6, 55·5	55·5	1·62	3	0·54
E	1·0	69·0, 69·3, 70·8, 70·9	70·0	2·94	3	0·98
F	1·2	86·0, 84·8, 84·0, 83·2	84·5	4·28	3	1·43
Total			53·0	12·06	18	0·67

Standard deviation, 0·82; Coefficient of variation, 1·5%

method was found to be satisfactory, with a standard deviation $s = 0{\cdot}82$ and coefficient of variation of 1·5%.

Non-integrated response. Figure 6 is a typical recording of the non-integrated current response, obtained with hydrogen peroxide bleach standards. The results are summarized in Table IV. The same samples were used as for the integrated method. A rectilinear relationship between signal and concentration is again obtained. The reproducibility of this method was found to be slightly better than that of the integrated method, with $s = 0{\cdot}58$ and coefficient of variation 1·0%.

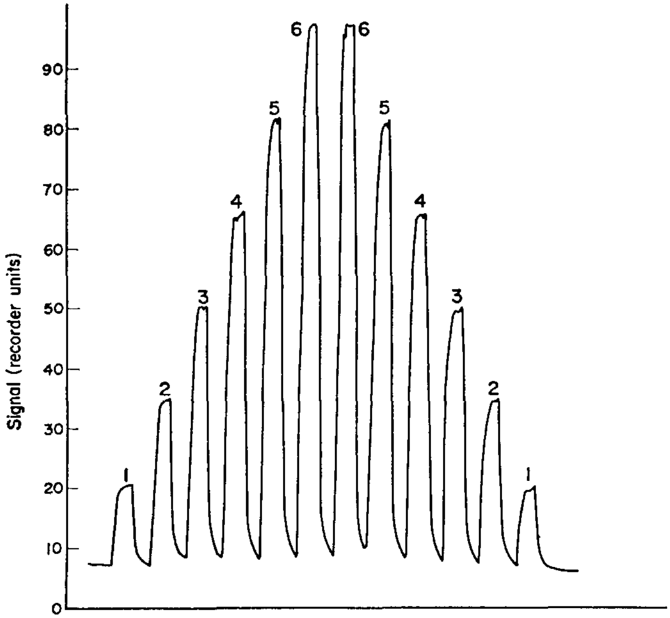


Fig. 6.—Non-integrated signals obtained for the hydrogen peroxide method. Sample concentration: 1, 0·20; 2, 0·40; 3, 0·60; 4, 0·80; 5, 1·00; 6, 1·20 volume H_2O_2.

Continuous monitoring vs. *semicontinuous monitoring.* As discussed above, the integrated method should be used in the analysis of discrete samples whereas the non-integrated method should be used in continuous monitoring and control. Drastic

Table IV.—Non-integrated response at varying concentrations of hydrogen peroxide. A statistical evaluation of the results obtained

Sample	Conc. of sample *Volume* H_2O_2	Non-integrated response (results of replicate analyses) *Recorder units*	Mean	Sum of squares	Degree of freedom	Variance
A	0·2	20·0, 20·5, 19·8, 19·7	20·0	0·38	3	0·13
B	0·4	34.0, 35·1, 34·3, 34·6	34·5	0·66	3	0·22
C	0·6	49·5, 49·5, 48·8, 50·2	49·5	0·98	3	0·33
D	0·8	64·2, 64·5, 65·8, 65·5	65·0	1·87	3	0·66
E	1·0	81·0, 81·3, 81·5, 80·2	81·0	0·98	3	0·33
F	1·2	96·3, 97·0, 97·1, 95·7	96·5	1·29	3	0·43
Total			57·6	6·07	18	0·337

Standard deviation 0·58; coefficient of variation, 1·0%

fluctuations in bleach liquor concentrations are, however, rarely observed in bleach baths, which normally show a gradual drift towards lower concentrations. Minute-to-minute close control of the bleach liquor concentrations is, therefore, often superfluous, and a less rigorous form of continuous monitoring would be sufficient. Fleet *et al.*[12] have recently described a semicontinuous form of monitoring in which a constant sample stream is introduced while the reagent, interspersed with water wash, is supplied from a standard sampler. A series of current-time waves would be obtained which would vary in height with any change in the concentration of the sample. Figure 7 is a typical recording of the signals obtained when the potassium periodate reagent was supplied at the rate of 10/hr (1:1 wash ratio). The first four waves correspond to signals obtained when a continuous stream of a 0·4 volume hydrogen peroxide bleach standard was supplied. The next two sets of four waves correspond to continuous

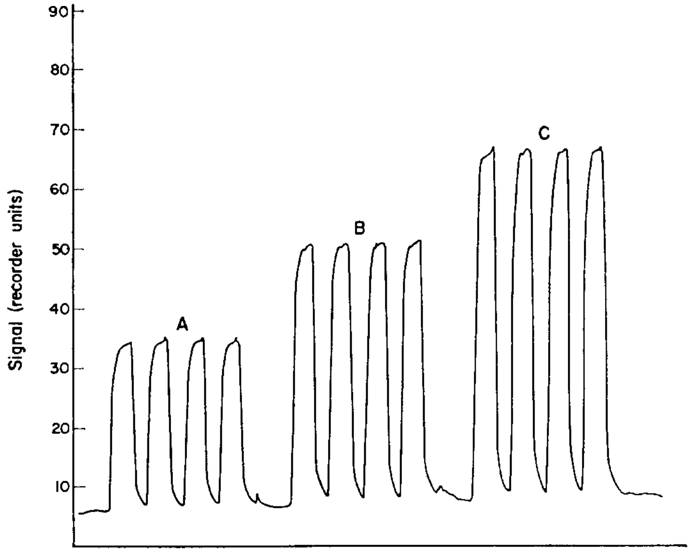


Fig. 7.—Current-time waves obtained when the hydrogen peroxide sample was continuously supplied whereas the potassium periodate reagent was supplied at the rate of 10/hr., interspersed with water wash at a ratio of 1:1. Sample concentration *A*, 0·40; *B*, 0·60; *C*, 0·80 volume H_2O_2.

streams of 0·6 and 0·8 volume hydrogen peroxide bleach standards respectively. By use of this semicontinuous method, the cost of the reagent is reduced by half and the response is easier to interpret since a definite step is obtained rather than a continuous record. Although only 10 readings are obtained per hour, that should be sufficient for bleach liquor control purposes

Dynamic response of the system. As discussed in the hypochlorite method, it is the total response time—dead-time plus transition time—which is important in continuous monitoring. The dynamic response of the system is assessed in the same way as described above. The dead-time of the system was found to be 2¾ minutes for a change in concentration equal to 0·2 volume hydrogen peroxide.

Conclusion

The dual objective of an ideal bleaching process—an excellent white with no significant damage to the textile material—can only be achieved by close control of the bleaching bath, its contents and conditions. The automated methods described in the present work enable one of these parameters, the bleach-bath concentration, to be effectively controlled and hence would be useful in the textile industry.

Acknowledgement—One of us (A. Y. W. Ho) thanks the Association of Commonwealth Universities for the award of a research grant. The authors also gratefully acknowledge the financial assistance of the Technicon Corporation.

Zusammenfassung—Ein neues Verfahren zur automatischen Bestimmung von Natriumhypochlorit und Wasserstoffperoxid wird beschrieben; es beruht auf der Verwendung einer porösen katalytischen Silberelektrode. Das Prinzip beider Methoden besteht in der quantitativen Freisetzung von Sauerstoff, der coulometrisch an der Elektrode gemessen wird. Die Vorschriften sind zur kontinuierlichen Gehaltskontrolle von Bleichbädern geeignet.

Résumé—On décrit une nouvelle voie d'accès au dosage automatisé de l'hypochlorite de sodium et de l'eau oxygénée, basée sur l'emploi d'une électrode d'argent catalytique poreuse. Le principe des deux méthodes comprend la libération quantitative de l'oxygène, qui est mesuré coulométriquement par l'électrode. Les techniques conviennent au contrôle continu des teneurs de bains de blanchiment.

REFERENCES

1. A.S.T.M. Designation D919-49, *Test for Copper Number of Paper and Paperboard, Book of A.S.T.M. Standards* 1969, **15**, 319.
2. A.S.T.M. Designation D539-53, *Test for Apparent Fluidity of Dispersions of Cellulose Fibres, ibid.*, 1969, **25**, 86.
3. B. S. 2610, *Method for determining the Fluidity of Cotton, Rayons and Cellulose Acetate in Cuprammonium Hydroxide Solution*, B.S.I., 1955.
4. A.S.T.M. Designation D1696-61, *Test for Solubility of Cellulose in Sodium Hydroxide, Book of A.S.T.M. Standards*, 1969, **15**, 571.
5. W. Garner, *Textile Laboratory Manual*, p. 41. National Trade Press, London, 1951.
6. C. R. Nodder, *J. Textile Inst.*, 1931, **22**, 416.
7. J. T. Marsh, *An Introduction to Textile Bleaching*, Chapman & Hall, London, 1946.
8. E. R. Trotman, *Dyeing and Chemical Technology of Textile Fibres*, p.205. Griffin, London, 1964.
9. M. H. Adelman and R.L. Pellissier, *Automation in Analytical Chem. Technicon Symposia* 1965, p. 183. Mediad, New York, 1966.
10. J. Tenygl, B. Fleet and A. Y. W. Ho, *Anal. Chem.*, in the press.
11. *Idem, Nature*, in the press.
12. B. Fleet, A. Y. W. Ho and J. Tenygl, *Analyst*, in the press.
13. *Idem, J. Clin. Chem.*, in the press.
14. Ridge and Little, *J. Textile Inst.*, 1942, **33r**, 59.
15. Laporte Ltd., *Bleaching Manual*, quoted in ref. 8.

Talanta, 1972, Vol. 19, pp. 329 to 340. Pergamon Press. Printed in Northern Ireland

STUDY OF OXIDATION STATE OF PLUTONIUM IN SOLUTION BY FLOW-COULOMETRIC METHOD

SORIN KIHARA, TADASHI YAMAMOTO and KENJI MOTOJIMA
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan

TAITIRO FUJINAGA
Department of Chemistry, Faculty of Science Kyoto University, Kitashirakawa, Sakyo-ku
Kyoto, Japan

(*Received* 12 *November* 1970. *Revised* 25 *April* 1971. *Accepted* 21 *June* 1971)

Summary—Reduction rates of Pu(IV) and oxidation rates of Pu(III) have been studied in sulphuric acid and nitric acid media, as functions of acid concentration, plutonium concentration and kind of acid. A flow-coulometric method was used in this work. This procedure has many merits, namely, the sample size required is very small, special reagents are not used, fewer limitations are imposed by the type and concentration of acid, and the method is rapid.

PLUTONIUM exists in aqueous solution as Pu^{3+}, Pu^{4+}, PuO_2^+ and PuO_2^{2+}. The standard oxidation-reduction potentials of their couples are close to each other,[1] so disproportionation reactions occur easily. It is reported that the oxidation of Pu^{3+} occurs in the presence of oxygen.[2] Up to the present, the oxidation states of plutonium in solution have been studied by solvent extraction, co-precipitation or spectrophotometric measurement of special ionic species. However, extraction or co-precipitation methods have many disadvantages:

(1) the oxidation state may be changed by chemical reaction between plutonium and the reagent added;
(2) the acid concentration must be chosen in a limited range and a certain kind of acid must be employed;
(3) the operations require a time ranging from 10 min to a few hours.

On the other hand, spectrophotometric methods are excellent for identification of the oxidation states, but useful only when plutonium concentrations are relatively high. In this work, a flow-coulometric method which was investigated by Fujinaga and others[3] has been used to study oxidation states of plutonium in sulphuric and nitric acid media. This method has the following merits:

(1) the sample size required is 10–50 μl,
(2) limitations imposed by acid concentrations, kind of acid, or plutonium concentrations are fewer than in other methods,
(3) special solvents or co-precipitants are not needed, so the side-reactions with plutonium cannot occur,
(4) the time needed is only a few minutes.

In this work, we were concerned with the behaviour of Pu^{3+} and Pu^{4+} in the sulphuric or nitric acid media which are commonly used in solution chemistry and studied correlations between the concentrations of acid or plutonium and transformation of the oxidation states. Such correlations for perchloric and hydrochloric acid media have been studied by Rabideau,[4] Rabideau and Cowan,[5] and Connick and McVey,[6] and in nitric acid media by Artyukin *et al.*[7]

EXPERIMENTAL

Reagents

Plutonium metal. A product of Nuclear Materials and Equipment Co., U.S.A., was used. Its isotopic composition was ^{239}Pu 91·3, ^{240}Pu 7·81, ^{241}Pu 0·85, ^{242}Pu 0·04 atom %.

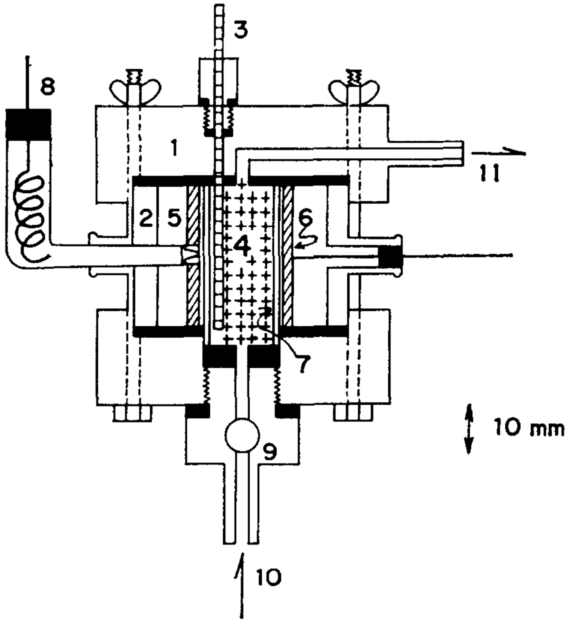


FIG. 1.—Electrolytic cell.

(1) Teflon (2) Glass cylinder
(3) Glassy carbon lead
(4) Glassy carbon grains (working electrode)
(5) Saturated KCl solution
(6) Glassy carbon cylinder (counter electrode)
(7) Porcelain cylinder (8) Ag–AgCl reference electrode
(9) Sample inlet (10) Supporting electrolyte inlet
(11) Supporting electrolyte outlet
▬ Silicone rubber.

Plutonium sulphate solutions. Plutonium metal was dissolved in 0·5*M* sulphuric acid after electrorefining and weighing.

Plutonium nitrate solutions. Plutonium metal was dissolved in 1·0*M* hydrochloric acid. The plutonium chloride solution was evaporated almost to dryness at 100–150°. Small amounts of 1·0*M* nitric acid were added to the residue and evaporated almost to dryness at 100–150°; this procedure was repeated three times. The final nitrate solution was prepared by dissolving the residue with 1·0*M* nitric acid.

From the results of colorimetry and coulometry plutonium is expected to be present as a mixture of Pu(IV), Pu(III) and a negligibly small amount of Pu(VI) in both sulphuric and nitric acids immediately after the above-mentioned preparation procedures.

The oxidation state of plutonium is adjusted by batch electrolysis with a glassy carbon[8] working electrode, just before measurements.

All other reagents used were of extra-pure grade.

Apparatus

An electrolytic cell for flow-coulometry is shown in Fig. 1. Glassy carbon grains (80–100 mesh), which act as a working electrode, are packed in a 7-mm bore porcelain cylinder, which is the electrolytic diaphragm. A glassy carbon cylinder is used as the counter electrode and the silver–saturated silver chloride electrode (SSE) is used as the reference electrode. The supporting electrolyte, the acid solution, flows from the supporting-electrolyte solution reservoir to the drain tank *via* the sample injection port and working electrode. Sample solutions are injected by a micro-syringe or through a rotating cock from the sample injection port. The supporting electrolyte flows through 3-mm vinyl tubing.

A Hokuto Denko Co. model PS-500B potentiostat was used. The current-time curve of electrolysis was recorded by a Yokogawa Electric Works type 3047 recorder. The current integration was made with a Koizumi Sokki Co. model KP-30 polar disk planimeter.

Pretreatment of glassy carbon electrode. The glassy carbon working electrode is oxidized at 1·2 V *vs.* SSE for 5 min and reduced at −1·0 V *vs.* SSE for the same time in 0·5*M* sulphuric acid or 1·0*M* nitric acid and this procedure is repeated five times.

Procedure

Flow-coulometric measurement. Supporting electrolyte (0·5*M* sulphuric acid for sulphate sample or 1*M* nitric acid for nitrate sample) is passed through the flow-coulometric column electrode, at a flow-rate of 5 ± 0·5 ml/min, regulated by varying the height of solution reservoir; the flow-rate is not critical (20% tolerance). The potential of the working electrode is adjusted to an appropriate value, then 10–50 μl of plutonium solution are injected and the current–time curve for electrolysis is recorded. The amount of plutonium electrolysed is determined by integrating the current–time curve and converting the number of coulombs into weight or concentration.

The supporting electrolyte and sample solution are not deaerated, for the following reasons: it was confirmed by preliminary experiments that there is no electrolytic reaction of air at the potential range used in this work, and for later practical application the behaviour of plutonium ions should be observed in the presence of oxygen.

Determinations are reproducible to within ±3% and blank corrections are not needed for more than 1 μg of plutonium. The total time required to determine the amount of plutonium (from sample injection to recording of current-time curve) is 10–40 sec, depending on the plutonium concentration.

RESULTS AND DISCUSSION

Plutonium in sulphuric acid solution

Voltage *vs.* quantity of electricity curves (*E–Q* curves) for the Pu(III)/Pu(IV) system in 0·5*M* sulphuric acid are shown in Fig. 2. Ten μl of 1·00 mg/ml plutonium solution (41·8 nmole of Pu) were taken each time. Curve 1 shows the reduction curve of Pu(IV) to Pu(III) obtained by varying the working potential of the flow-coulometric column electrode from +1·20 to −0·20 V *vs.* SSE. The Pu(IV) solution was prepared by batch electrolysis at +1·10 V *vs.* SSE. Similarly, curve 2 shows the oxidation curve of Pu(III) to Pu(IV). The Pu(III) solution was prepared by batch electrolysis at +0·30 V *vs.* SSE. Curve 3 shows the *E–Q* curve of plutonium that had been left for five months after the plutonium metal had been dissolved in 0·5*M* sulphuric acid.

It is confirmed by comparing curve 3 with curve 2 in Fig. 2 that the amount of Pu(VI) or Pu(V) is small (less than 2% of the total plutonium) in 0·5*M* sulphuric acid. The sum of the quantity of electricity (Q_3) for reduction at +0·35 V *vs.* SSE and that for oxidation at +0·75 V *vs.* SSE in curve 3 is nearly equal to the quantity of electricity (Q_2) at +0·75 V *vs.* SSE in curve 2. If Pu(VI) is present, Q_3 should be larger than Q_2 because, at +0·35 V *vs.* SSE, Pu(VI) should be reduced to Pu(III) and hence a three-electron change should be involved. The reason why Pu(VI) generated by disproportionation of Pu(IV) disappears is not clear. But it can be considered that the reduction of Pu(VI) by hydrogen peroxide[9,10] or α-ray direct reduction[11] and the complex-formation between Pu(IV) and sulphate make Pu(VI) unstable. Hydrogen

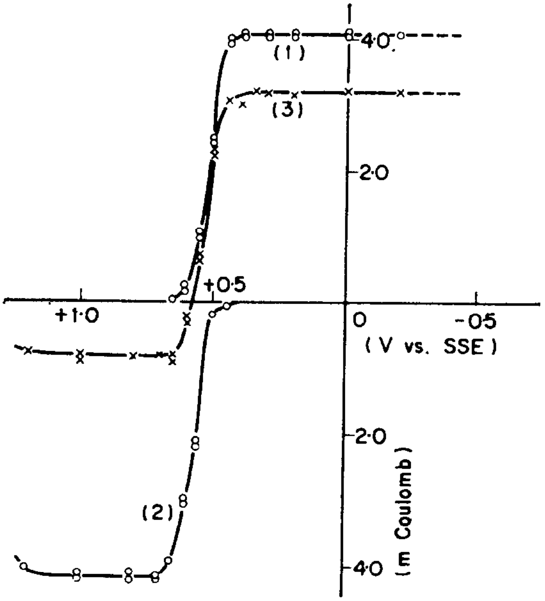


FIG. 2.—Coulomb-potential curves of plutonium.
Sample: 4·18 × 10^{-8} mole Pu;
Electrolyte: 0·5*M* H_2SO_4
(1) Pu(IV) + *e* = Pu(III)
(2) Pu(III) − *e* = Pu(IV)
(3) Mixture of Pu(III) and Pu(IV).
(The solution was left for five months after dissolution of the plutonium metal.)

peroxide is generated by radiolysis of water[10] or reduction of dissolved oxygen by Pu(III).[2] The formal oxidation-reduction potential of the H_2O_2/O_2 couple is +0·68 V and that of the Pu(IV)/Pu(VI) couple is between +1·2 and +1·4 V in 0·5*M* sulphuric acid at 25°.[1]

Plutonium in nitric acid solution

E–Q curves for the Pu(III)/Pu(IV) and Pu(III)/Pu(VI) couples in 1·0*M* nitric acid are shown in Fig. 3. Ten μl of 5·40 mg/ml plutonium solution (0·226 μmole of Pu) were taken in each case. Curve 1 shows the reduction curve of Pu(IV) to Pu(III) obtained by varying the column electrode potential from +1·20 to 0·00 V *vs.* SSE. Pu(IV) solution was prepared by batch electrolysis at +0·90 V *vs.* SSE. Similarly, curve 2 shows the oxidation curve of Pu(III) to Pu(IV). Pu(III) solution was prepared by batch electrolysis at +0·30 V *vs.* SSE. A comparison of the sum of the quantity of electricity at +0·30 and +1·20 V *vs.* SSE (Fig. 3) with the theoretical value indicates that the amount of Pu(VI) or Pu(V) is less than 2% of the total plutonium, in 1·0*M* nitric acid, immediately after preparation of the plutonium nitrate solution from chloride solution. After controlled potential electrolysis at +0·90 V *vs.* SSE, the quantity of electricity for reduction, at +0·30 V *vs.* SSE, is nearly equal to the theoretical value calculated for a one-electron reduction and it is estimated that almost all the plutonium is converted into Pu(IV) by controlled potential electrolysis.

Curve 3 shows the *E–Q* curve of plutonium that has been left for two months in

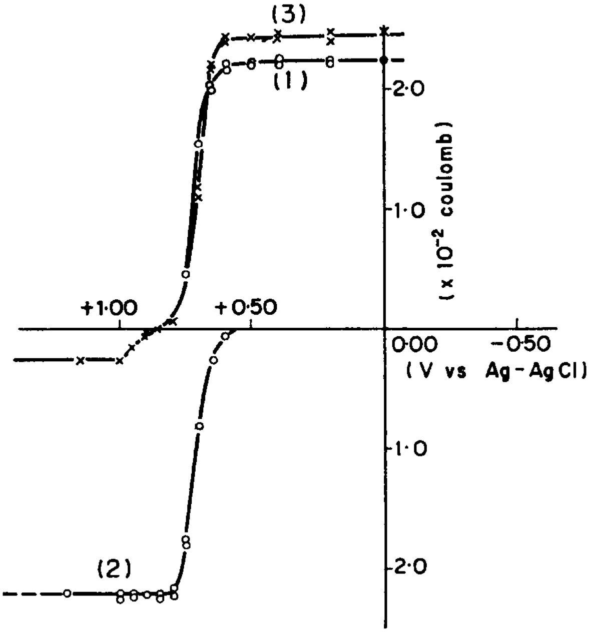


FIG. 3.—Coulomb-potential curves of plutonium
Sample: 10 μl of 5·40 mg/ml Pu (2·26 × 10^{-7} mole)
Electrolyte, 1·0*M* HNO_3; flow-rate, 5 ml/min.
(1) Pu(IV) + *e* = Pu(III). (2) Pu(III) − *e* = Pu(IV)
(3) Oxidation and reduction of Pu(III), Pu(IV) and Pu(VI) mixtures.
(The nitrate solution was left for two months after preparation.)

1·0*M* nitric acid. It was reported[7] that in 0·1–0·5*M* nitric acid Pu(III), Pu(IV) and Pu(VI) ions were generated by the disproportionation reaction

$$3\text{Pu(IV)} + 2H_2O \rightarrow 2\text{Pu(III)} + \text{Pu(VI)} + 4H^+. \qquad (1)$$

It is found, by comparing the quantity of electricity at +0·30 V *vs.* SSE (Q_1) in curve 1 with the quantity of electricity at +0·30 V *vs.* SSE (Q_{3-r}) and at +1·20 V *vs.* SSE (Q_{3-o}) in curve 3 that Pu(III), Pu(IV) and Pu(VI) ions are generated in 1·0*M* nitric acid medium. It can be considered that some of the Pu(III) is reoxidized to Pu(IV) by dissolved oxygen or nitrate, because Q_{3-r} is larger than Q_1. If only the reaction of equation (1) occurs, Q_{3-r} should be equal to Q_1. The amount of Pu(III) is calculated from Q_{3-o} to be 0·026 μmole and the amounts of Pu(VI) and Pu(IV) are calculated to be 0·024 and 0·176 μmole respectively:

$$\text{Pu(VI) (mole)} = \frac{1}{2}\cdot\frac{1}{96500}\left\{Q_{3-r}(\text{coul.}) - [Q_1(\text{coul.}) - Q_{3-o}(\text{coul.})]\right\} \qquad (2)$$

$$\text{Pu(IV)} = \text{total Pu} - \text{Pu(III)} - \text{Pu(VI)} \qquad (3)$$

In the study of oxidation of Pu(III), the concentration of dissolved oxygen was found to be 2–3 × 10^{-4}*M*, by a polarographic method. The concentration of oxygen was maintained constant by bubbling solution-saturated air through the sample solution. In the reduction study of Pu(IV), solutions were not deaerated and were allowed to stand in contact with air.

Reduction reactions of Pu(IV)

The disproportionation reaction, α-ray reduction, oxidation or reduction of reaction products by solvent or atmosphere, and complex-formation by Pu(IV) are the main factors in the rate of transformation of oxidation state of Pu(IV). It has been reported that the disproportionation reaction is the most important and rate-determining factor.[5,12]

In the present work, on the assumption that the rate of generation of Pu(III) is nearly proportional to the apparent rate of transformation of oxidation state of Pu(IV), the ratio of Pu(III) to total plutonium is plotted as a function of time.

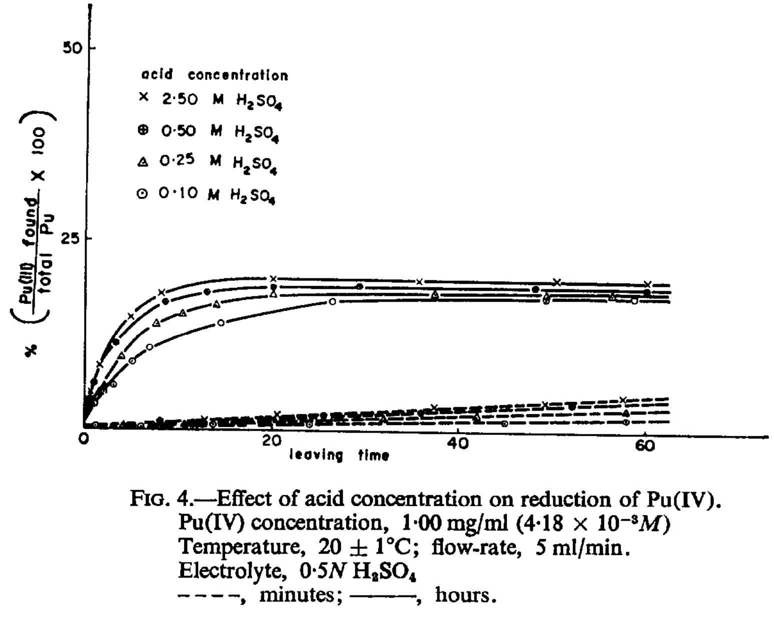


Fig. 4.—Effect of acid concentration on reduction of Pu(IV).
Pu(IV) concentration, 1·00 mg/ml ($4{\cdot}18 \times 10^{-3}M$)
Temperature, 20 ± 1°C; flow-rate, 5 ml/min.
Electrolyte, 0·5*N* H_2SO_4
– – – –, minutes; ———, hours.

The relationship between time and reduction of Pu(IV) at various sulphuric acid concentrations is shown in Fig. 4. The plutonium concentration was 1·00 mg/ml. Figure 4 shows that the higher the concentration of sulphuric acid, the larger the degree of reduction. After 30 hr, the equilibrium is nearly established and about 17–20% of Pu(IV) is reduced. The influence of plutonium concentration is shown in Fig. 5, for a concentration of sulphuric acid of 0·5*M*; the lower the plutonium concentration, the easier the reduction. At Pu = 1·00 mg/ml, only about 10% of Pu(IV) was reduced after 20 hr. Similar relationships for nitric acid medium are shown in Figs. 6 and 7.

Disproportionation reactions of Pu(IV) in perchloric or hydrochloric acid have been studied by Rabideau,[4] Connick and McVey[6] and other authors. For sulphuric or nitric acid media, however, data on transformation of the oxidation state of Pu(IV) are scarce. The disproportionation equilibrium constants $K = [\mathrm{Pu(III)}]^2[\mathrm{Pu(VI)}][\mathrm{H}^+]^4/[\mathrm{Pu(IV)}]^3$, were determined in 0·2–1·0*M* perchloric acid[4] and 0·2–1·0*M* hydrochloric acid.[6] In obtaining these results, the effects of the anion were not taken into account, and results on the relationship between disproportionation and time are insufficient. In the present work, however, it is found that transformation of the oxidation state of

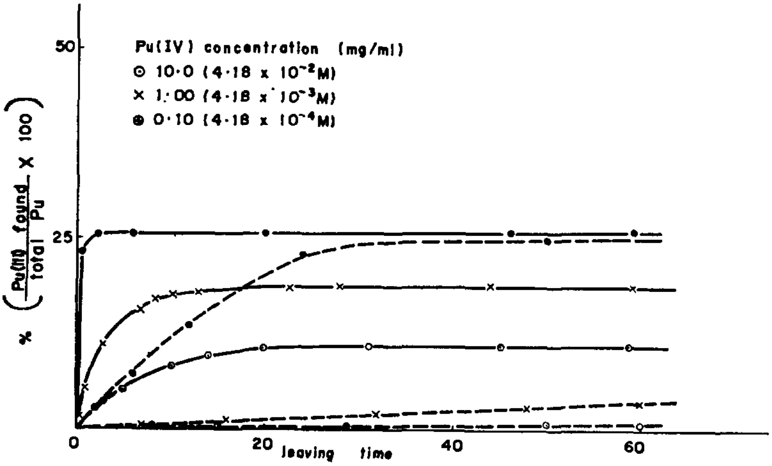


Fig. 5.—Effect of Pu(IV) concentration on reduction of Pu(IV). Acid concentration, 0·5M H_2SO_4, electrolyte; 0·5M H_2SO_4 Temperature, 20 ± 1°C: flow-rate, 5 ml/min. ----, minutes; ——, hours.

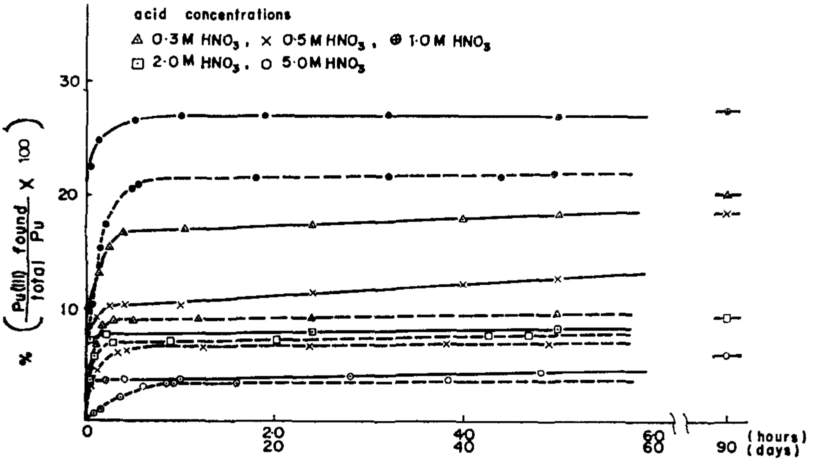


Fig. 6.—Effect of acid concentration on reduction of Pu(IV). Pu(IV) concentration, $1{\cdot}23_6$ mg/ml (5·17 × $10^{-3}M$) Temperature, 20 ± 1°C; flow-rate, 5 ml/min. Electrolyte: 1·0M HNO_3 ----, hours; ——, days.

Pu(IV) is scarcely affected by acid concentration in the range 0·1–2·5M sulphuric acid. On the other hand, the rate of transformation of the oxidation state of Pu(IV) decreases with increasing acid concentration in the range 1·0–5·0M nitric acid, and is also lower in 0·3–0·5M than in 1·0M nitric acid. It is considered that the oxidizing power of nitrate or nitrite ions may stabilize Pu(IV) at higher nitric acid concentration. In 0·5M sulphuric acid medium, the rate of transformation of oxidation state of Pu(IV) decrease with increasing plutonium concentration in the range 0·1–10 mg/ml. In nitric acid, however, plutonium concentrations in the range 0·332–1·24 mg/ml have

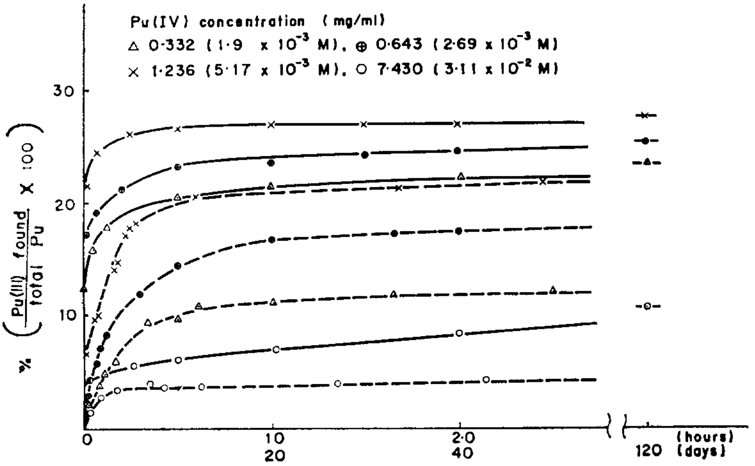


FIG. 7.—Effect of Pu(IV) concentration on reduction of Pu(IV). Acid concentration, 1·0*M* HNO_3; electrolyte, 1·0*M* HNO_3 Temperature, 20 ± 1°C; flow-rate, 5 ml/min. ----, hours, ———, days.

little influence on the transformation rate but at high plutonium concentration (7·43 mg/ml) Pu(IV) becomes more stable. Equilibrium is much more rapidly reached in sulphuric acid than in nitric acid, and takes longer with increasing concentration of plutonium and decreasing acid concentration.

From Figs. 4–7 it seems that transformation of Pu(IV) is induced by complexation reactions and that equation (1), obtained for perchloric, hydrochloric and 0·1–0·5*M* nitric acid media does not apply for the transformation in sulphuric and nitric acids.

In 0·5*M* hydrochloric acid, 0·002*M* plutonium solution (478 μg/ml) at 25° was found by Connick and others[13] to disproportionate to give about 26·3% Pu(III), 62·8% Pu(IV), 0·5% Pu(V) and 10·5% Pu(VI) at equilibrium. A 2 mg/ml solution of Pu(IV) in 0·5*M* nitric acid at 25° was found by Hall[14] to give 12% Pu(III), 66% Pu(IV) and 22% Pu(VI) at equilibrium. In the present study, in 0·5*M* nitric acid, 18·5% Pu(III), 68·8% Pu(IV) and 10·7% Pu(VI) were found for 1·24 mg/ml plutonium solution at equilibrium at 20°. Pu(IV) and Pu(VI) are calculated from the quantity of electricity used at +1·20 V and +0·30 V *vs.* SSE [equations (2) and (3)].

Oxidation reactions of Pu(III)

For the oxidation mechanism of Pu(III), it is supposed that dissolved oxygen plays an important role.[2] If the Pu(III) solution is deaerated by passage of pure nitrogen gas, the oxidation of Pu(III) solution is very slow and Pu(IV) cannot be detected after 6 hr, in either sulphuric or nitric acid. Pu(III) (1·0 mg/ml) in 0·5*M* sulphuric acid or 1·0*M* nitric acid were used in this study. In 1·0–5·0*M* nitric acid, however, nitrate or nitrite oxidation may be involved. Dukes[14] reported that in the presence of nitrite ion the oxidation of Pu(III) is faster in nitric acid than in perchloric or hydrochloric acid.

The relationship between time and oxidation of Pu(III) for different sulphuric acid concentrations is shown in Fig. 8. The concentration of plutonium was 50 μg/ml.

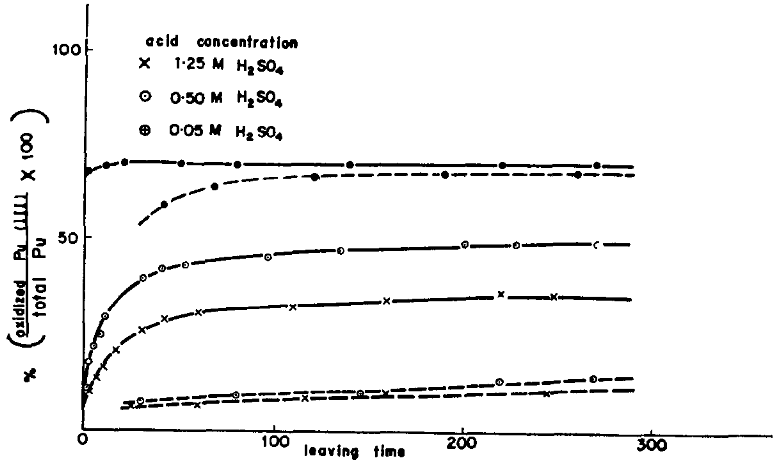


FIG. 8.—Effect of acid concentration on oxidation of Pu(III).
Pu(III) concentration, 50 μg/ml (2·09 × $10^{-4}M$)
Temperature, 20 ± 1°C; flow-rate: 5 ml/min.
Electrolyte, 0·5N H_2SO_4
– – – –, seconds; ———, minutes.

Figure 8 shows that the lower the acid concentration, the more easily the oxidation of Pu(III) occurs. In 0·05M sulphuric acid, the equilibrium of Pu(III)/Pu(IV) is established immediately, but in 1·25M sulphuric acid about 2 hr is needed. The effect of plutonium concentration is shown in Fig. 9. The concentration of sulphuric acid was 0·5M. Figure 9 shows that the lower the plutonium concentration, the easier the oxidation of Pu(III). Pu(III) oxidizes rapidly within the first 1 hr and then slowly to equilibrium. After 10 hr, in the case of 50 μg/ml Pu, about 55% of Pu(III) is oxidized, but in the case of 10 mg/ml, only 12%.

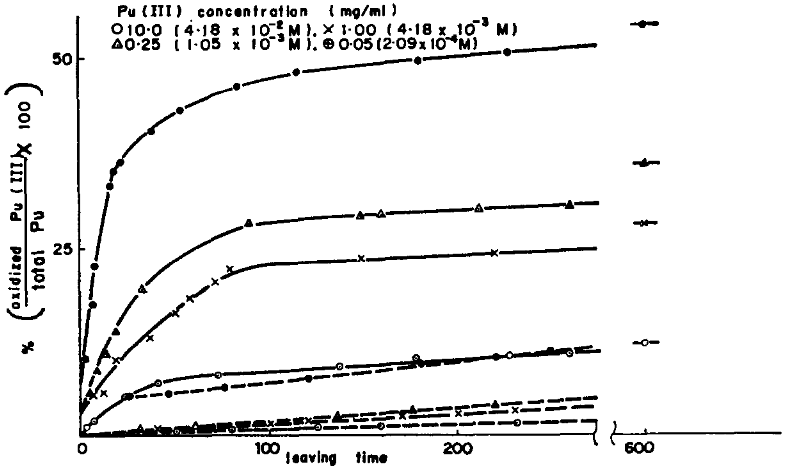


FIG. 9.—Effect of Pu(III) concentration on oxidation of Pu(III).
Acid concentration, 0·5M H_2SO_4; electrolyte, 0·5M H_2SO_4
Temperature, 20 ± 1°C; flow-rate, 5 ml/min.
– – – –, seconds; ———, minutes.

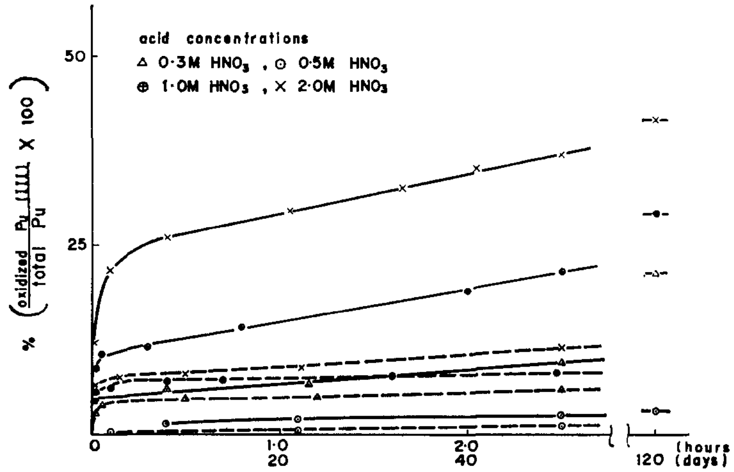


FIG. 10.—Effect of acid concentration on oxidation of Pu(III).
Pu(III) concentration, $1{\cdot}23_8$ mg/ml ($5{\cdot}17 \times 10^{-3}$*M*)
Temperature, 20 ± 1°C; flow-rate, 5 ml/min.
Electrolyte, 1·0*M* HNO_3
– – – –, hours; ———, days.

Similar relationships for nitric acid media are shown in Figs. 10 and 11. Figure 10 shows that in 0·5*M* nitric acid the oxidation of Pu(III) (1·24 mg/ml) is at a minimum and even after 120 days only 3% of Pu(III) is oxidized. When the nitric acid concentration is more than 5·0*M*, Pu(III) is oxidized to Pu(IV) as soon as the pre-electrolysis is stopped, because nitrite ion is generated in the solution by the pre-electrolysis. Figure 11 shows that when the plutonium concentration is 1·24 mg/ml (in 1·0*M* nitric acid), the oxidation is slowest and at higher plutonium concentration the equilibrium

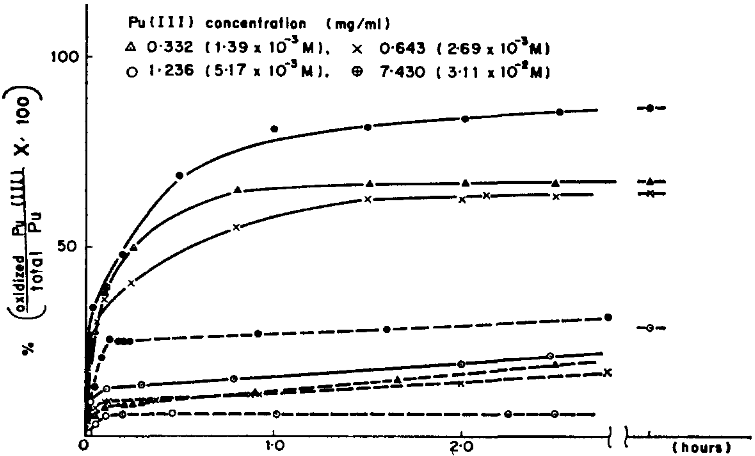


FIG. 11.—Effect of Pu(III) concentration on oxidation of Pu(III).
Acid concentration, 1·0*M* HNO_3; electrolyte, 1·0*M* HNO_3
Temperature, 20 ± 1°C; flow-rate, 5 ml/min.
– – – –, hours: ———, days.

is established more quickly. It was confirmed that the amount of Pu(VI) generated from oxidized Pu(IV) was negligible.

In both $0{\cdot}5M$ sulphuric acid and $1{\cdot}0M$ nitric acid, oxidation of Pu(III) becomes faster with decreasing plutonium concentration, but in $1{\cdot}0M$ nitric acid at a relatively high plutonium concentration (7·43 mg/ml), an extremely large fraction of Pu(III) is oxidized. The rate of oxidation of Pu(III) decreases with increasing acid concentration in $0{\cdot}3$–$0{\cdot}5M$ nitric acid and $0{\cdot}05$–$1{\cdot}25M$ sulphuric acid. In $1{\cdot}0$–$5{\cdot}0M$ nitric acid, on the contrary, the rate of oxidation increases with acid concentration. Pu(III) may be oxidized by nitrate, nitrite and dissolved oxygen at higher nitric acid concentrations.

The oxidation mechanism of Pu(III) in sulphate media was discussed by Newton and Baker.[2] They reported that 58·5% of Pu(III) was oxidized after 100 min under the following conditions; temperature 25°, $P_{O_2} = 750$ mbar, total Pu $= 5{\cdot}36 \times 10^{-3}M$, $0{\cdot}3M$ $HClO_4$, $0{\cdot}4M$ Na_2SO_4. In the present work, 23·1% of Pu(III) was oxidized after 100 min under the conditions; 20°, $P_{O_2} = 200$ mbar, total Pu $= 4{\cdot}18 \times 10^{-3}M$, $0{\cdot}5M$ H_2SO_4.

Oxidation of Pu(III) in sulphuric acid is much faster than in nitric acid. It is known that the oxidation is very slow in solutions of hydrochloric and perchloric acids.[12] The potential for oxidation of Pu(III) to Pu(IV), complex-formation of the anion with Pu(IV) and the oxidizing potential of the medium may affect the oxidation rate of Pu(III).

In the present work, apparent transformations of Pu(IV) and Pu(III) are studied, but more detailed studies are required to elucidate the mechanisms of these reactions.

Acknowledgement—The authors thank Dr. H. Onishi and Mrs. N. Tamura for their helpful discussions.

Zusammenfassung—Die Reduktionsgeschwindigkeit von Pu(IV) und die Oxidationsgeschwindigkeit von Pu(III) wurden in schwefelsaurem und salpetersaurem Medium in Abhängigkeit von Säurekonzentration, Plutoniumkonzentration und Art der Säure untersucht. Es wurde eine durchflußcoulometrische Methode verwendet. Sie hat viele Vorteile: man braucht nur sehr kleine Proben, es werden keine speziellen Reagentien verwendet, die durch Art und Konzentration der Säure gegebenen Einschränkungen sind geringer, und die Methode geht rasch.

Résumé—On a étudié les vitesses de réduction de Pu(IV) et les vitesses d'oxydation de Pu(III) en milieux acide sulfurique et acide nitrique, en fonction de la concentration de l'acide, de la concentration du plutonium et de la nature de l'acide. On a utilisé dans ce travail une méthode coulométrique par écoulement. Cette technique a de nombreux avantages, la prise d'essai nécessitée est très petite, on n'utilise pas de réactifs spéciaux, moins de limitations sont imposées par le type et la concentration de l'acide, et la méthode est rapide.

REFERENCES

1. W. M. Latimer, *Oxidation Potentials*, 2nd Ed., Prentice-Hall, New York, 1952.
2. T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1956, **60**, 1417.
3. T. Fujinaga, *Electrolytic Chromatography and Coulometric Detection with the Column Electrode Pure and Applied Chemistry*, Vol. 25, p. 709, Butterworths, London, 1971; T. Fujinaga, K. Izutsu and S. Okazaki, *Rev. Polarog.* (*Kyoto*), 1967, **14**, 164.
4. S. W. Rabideau, *J. Am. Chem. Soc.*, 1953, **75**, 798.
5. S. W. Rabideau and H. D. Cowan, *ibid.*, 1955, **77**, 6145.
6. R. E. Connick and W. H. McVey, *ibid.*, 1953, **75**, 474.
7. P. I. Artyukhin, V. I. Medvedovskii and A. D. Gel'man, *Russ. J. Inorg. Chem.*, 1959, **4**, 596.
8. S. Yamada and H. Sato, *Nature*, 1962, **193**, 261.
9. M. Pages, *J. Chem. Phys.*, 1962, **59**, 63.

10. C. B. Senvar and E. J. Hart, *Proc. of U.N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, 1958, **29**, 19.
11. M. Pages and M. Haissinsky, *ibid.*, 1958, **29**, 44.
12. J. M. Cleveland, *Plutonium Handbook*, Vol. 1, p. 403. Gordon and Breach, New York, 1967.
13. R. E. Connick, M. Kasha, W. H. McVey and G. E. Sheline, *The Transuranium Elements, National Nuclear Energy Series IV 14-B*, p. 559–601. McGraw-Hill, New York, 1949.
14. G. R. Hall, unpublished work, cited in J. G. Cunninghame and G. L. Miles, *J. Inorg. Nucl. Chem.*, 1956, **3**, 54.
15. E. K. Dukes, *J. Am. Chem. Soc.*, 1960, **83**, 9.

Talanta, 1972, Vol. 19, pp. 341 to 345. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF 0–50 ng OF CHROMIUM IN 1 ml OF HUMAN SERUM

J. AGTERDENBOS, L. VAN BROEKHOVEN, B. A. H. G. JÜTTE and J. SCHURING
Analytisch-Chemisch Laboratorium, Rijksuniversiteit, Croesestraat 77A,
Utrecht, Holland

(*Received* 27 *August* 1971. *Accepted* 25 *October* 1971)

Summary—A method is described for the determination of chromium in 1 ml of human serum or plasma. It is based on a wet decomposition and a spectrophotometric determination with diphenylcarbazide after extraction with methyl isobutyl ketone. A 40-mm cuvette with less than 1 ml sample volume is described. Results are lower than expected from the literature, most samples from healthy persons containing less than 2 or 3 ng/ml. The reproducibility is about 1 ng/ml.

IN MANY BIOLOGICAL systems chromium is present, generally in extremely low concentrations. In the last two decades the functions and occurrence of chromium in these systems have been extensively studied. A comprehensive survey of this work has been given recently by Mertz.[1] It shows that chromium probably plays a role in biological processes in human beings. Some points are that the element is accumulated in high concentrations in certain areas of the brain, in nucleic acids and in hair, and that during the first weeks or months of life, the chromium concentration in many organs is higher than for the rest of life. Correlation may exist between certain diseases and the chromium content of human tissues and organs. Plasma undergoes significant changes in chromium content after an oral glucose load.

Mertz[1] reports values for the chromium concentration in blood (or serum or plasma) ranging from 0 to 520 ng/ml, and concludes that most of the values are between 20 and 50 ng/ml, and that plasma chromium levels considerably below 20 ng/ml may be suggestive of a low dietary intake, but do not necessarily mean chromium deficiency. Niedermeier *et al.*[2] recently described a direct-reading emission spectrographic method. They report that 50% of the 105 sera analysed have a chromium content below their detection-limit of 10 ng/ml. They report a mean value of 30 ng/ml.

In order to make further studies of the subject, further development of analytical methods is necessary, however. If these methods have to be applied in clinical laboratories they have to be performed with apparatus generally available there. In the present work the possibility of the development of such a method, applicable to the determination of chromium in 1 ml of human serum, was studied. Of the techniques used for the determination of metals at such levels, emission spectrography is not sensitive enough (except perhaps if special techniques[2] are used) and it is not available at most clinical laboratories. The latter objection may also be made against X-ray fluorescence. This technique was used by Beyermann *et al.*[3] for the determination of chromium in urine (down to 15 ng) after extraction with 8-quinolinol into chloroform. The use of atomic absorption for purposes similar to ours was described by Feldman *et al.*[4,5] but it seems not sensitive enough (down to 30 ng) for the present problem. Volatile metal chelates have recently been used for the determination of metals in the subnanogram range. Measurements were made with gas chromatographs (with electron-capture detectors) and with mass spectrometers. The latter method has not so far been applied to practical problems of a similar nature to ours. The chromium content of the plasma of rats has been measured by GLC, but the animals had been injected with Na_2CrO_4 and the chromium content was about 50 ng/ml (Hansen *et al.*[6]).

A technique readily available in clinical laboratories is spectrophotometry, and therefore we tried to find a procedure using this technique. Except for some catalytic procedures which we did not study, the diphenylcarbazide reaction with chromium(VI) combined with methyl isobutyl ketone (MIBK) extraction seemed the most sensitive. Its application has often been described, *e.g.*, by Koch and Koch-Dedic,[7] Beyermann,[8] and Morsches and Tölg.[9] The method of decomposition entailed some modifications to the method of determination, which may be useful in other applications, too. Suitable apparatus is present in many clinical laboratories, except perhaps the cuvettes and the slit-attachment which may, however, be obtained commercially.

EXPERIMENTAL

Apparatus and reagents

Absorption measurements were made with the Uvispek H 700 (Hilger and Watts) with a slit-attachment H 742. A cuvette was made from a 50 × 34 × 12 mm Teflon block. A groove was milled, 17 mm deep, 36 mm long, and 2 mm wide. In both side-walls at the end of the groove a circular hole was drilled, the holes were threaded, and a perforated screw was placed in each hole (perforation 5 mm diameter). Quartz windows were placed in the holes and Buna-N O-rings used for sealing. The optical path was about 37 mm, the volume used for measurements about 0·9 ml. The H 742-slit was used with an aperture 2 mm high and 1 mm wide. Small volume 40-mm cuvettes are commercially available.

Pyrex and quartz tubes with glass stoppers were used both for sample decomposition and centrifugation. They were 15 mm in bore and 100 mm long and were heated in a copper block, in holes (6 in the block) with the proper diameter and about 20 mm deep. The block contained a small hole for a thermometer and was heated on an electric plate. A quartz tube, 3 mm outer and 1 mm inner diameter and 120 mm long, was sealed 2 mm above one of its ends and placed in the decomposition tube as a "stirring rod" to prevent bumping.

Doubly distilled demineralized water, distilled acetone, distilled methyl isobutyl ketone and "Suprapur" (Merck) acids were used, except for hydrochloric acid which was prepared by isothermic distillation.[10] The dichromate standard (100 μg/ml) was made from solid $K_2Cr_2O_7$; more dilute solutions were prepared daily. A chromium(III) solution was prepared from this standard by reduction with alcohol and sulphuric acid. Diphenylcarbazide solution (50 mg/25 ml) in MIBK was prepared fresh every week. MIBK–hydrochloric acid mixture was prepared by diluting 1 ml of 10*M* hydrochloric acid to 100 ml with MIBK. The decomposition mixture was prepared from nitric acid (65%) perchloric acid (70%) and sulphuric acid (96%) in the volume-ratio 3:1:1.

Procedure

Take a 1·0-ml sample in the decomposition tube, add 1·0 ml of the decomposition mixture, mix, add a stirring rod. Place the tubes in the block (at 60–70°) and after 5 min mix the foam formed with the rest of the contents. Heat the block to 90° in 25 min, then in 20 min more to 120° for the dissolution, in another 30 min to 150° for the predecomposition, in the next 45 min to 275° for the final decomposition and in 15 min to 330° for the removal of perchloric acid. Remove the tubes from the block and cool them. If the contents are yellow, heat again at 330° for 5 min.

Wash the wall and the stirring-rod each with 0·5 ml of 0·12*M* perchloric acid, add 0·2 ml of 0·01*M* potassium permanganate and place for 5 min on a water-bath (100°). Cool in ice, add 0·10 ml of 10*M* hydrochloric acid, keep at 0° until the permanganate colour disappears, add 1·00 ml of MIBK–hydrochloric acid solution (at 0°), extract for 1 min and then immediately centrifuge for 1 min at 2000 rpm. Take 0·85 ml of the organic phase in another centrifuge tube, add 0·10 ml of diphenylcarbazide solution, 0·01 ml of MIBK–hydrochloric acid solution and 0·10 ml of acetone. Mix, place in the dark, and measure the absorbance against water at 540 nm in a 40-mm microcuvette between 20 and 30 min after addition of the diphenylcarbazide. Substract the value of a blank obtained in the same way without the addition of serum.

Calibration curves without preliminary decomposition are prepared by the same procedure. Aliquots of a dichromate solution containing 0–100 ng of chromium are used, 0·2 ml of 96% sulphuric acid and 1 ml of 0·12*M* perchloric acid are added and the volume is adjusted to about 1·2 ml before the oxidation with permanganate.

DISCUSSION

The decomposition mixture described was also used by Feldman *et al.*[5] Its advantage over some other mixtures tried is that a small and constant amount is used. This eliminates the influence of impurities in the reagents. Moreover the decomposition does not take much work. There was some indication that blanks obtained with Pyrex tubes were slightly higher than those with quartz tubes but the difference—if any—was small. New tubes may cause loss of some chromium when first used. The oxidation of chromium(III) to chromium(VI) and the extraction with hydrochloric acid and MIBK (as $HCrO_3Cl.2MIBK$) have been described with slight variations by several others.[4,5,7,8,9,11]. Some of these authors[7,8,9] also describe the photometric determination. The method is very selective[8] and therefore not much work was done to investigate interferences. An exception was made for iron but at the levels normally present in serum the absorbance due to the iron contribution was found to be roughly equivalent to that of 0·1 ng of chromium.

Preliminary experiments gave some irregular results which suggested that perchloric acid left on the walls of the decomposition tube might affect the absorbance. It was found in experiments without the decomposition step that the addition of perchloric acid greatly enhanced the absorbance. Addition of 10 μl of 70% perchloric acid gave a constant and maximum absorbance value. Therefore the walls and the stirring rod were rinsed with the equivalent of this amount of acid. The rinsing with perchloric acid greatly improved the reproducibility of the complete procedure. Another modification is the addition of 0·1 ml of acetone to the organic phase. This addition prevents turbidity in the coloured solution.

For the blanks a mean value of zero was expected, and was found in about half the experiments, but all the others gave high blanks. The results suggest that the equivalent of 4 (or 2) ng of chromium are introduced in part of the experiments, but not in others. Statistical conclusions based on the Gaussian curve may therefore be incorrect. The mean value of the blanks is 1·4 ng, the standard deviation is 1·6 ng. This value is higher than the value of 1·0 ng found for the standard deviation in the measurement of samples, but it should be noted here that duplicate or triplicate samples were always analysed within one day, whereas the blanks were taken over a period of more than a week. The recovery experiments show recoveries of 96%, 103%, 93% and 94% (mean 97%) if a blank of 1·4 ng is substracted.

A calibration curve for the range 0–100 ng of chromium, obtained without application of the decomposition mixture and procedure, was linear, obeying the equation $1000A = 2{\cdot}16x + 1{\cdot}7$, where A was the absorbance and x the number of ng of chromium. A similar curve prepared with 1 ml of a serum and 0–50 ng of chromium was also linear, with the equation $1000A = 2{\cdot}15x + 8{\cdot}4$. The standard deviation was 0·6 ng in both cases.

From the analytical point of view it is concluded that the procedure described allows the determination of chromium in serum or plasma at the 0–50 ng level with a standard deviation of about 1 ng, but that blanks and samples should preferably be run at the same time. Fourteen experiments a day are possible.

BIOCHEMICAL APPLICATION

A total of 27 heparinized plasma samples and 10 sera samples from healthy adults were analysed for chromium, with the results given in Table I. Youden's formulae[12] were used to determine the standard deviations.

TABLE I.—CHROMIUM CONTENT OF THE SERUM OF 37 HEALTHY PERSONS FROM UTRECHT AND ROTTERDAM, AND RESULTS OF 14 BLANKS.

Cr found, *ng/ml*	Number of persons*	Number of blanks†
<1	3	7
1	10	1
2	16	2
3	2	0
4	1	4
5	4	0
6	1	0

* Most results were mean values for two (or three) analyses.

† Single experiments.

Most of the values given for the samples in the table are mean values of duplicate experiments; in a few cases only a single determination was made, in a few others triplicate experiments were run. From each set of duplicate or triplicate experiments (made on the same day) the standard deviation was calculated and a pooled value of 1·0 ng/ml was found with 31 degrees of freedom. No differences due to age or sex could be detected in the results. No difference was found between serum and plasma. Twelve blanks (including decomposition) and four recovery experiments were also run. Results for the blanks are given in Table I. Recovery experiments with 10 or 20 ng of Cr(VI) and 20 or 40 ng of Cr(III) gave measured values of 11, 22, 20 and 39 ng respectively. From a biochemical point of view we have to conclude that results for healthy persons are lower than might be expected from the review of Mertz[1] and the work of Niedermeier *et al.*[2] The best conclusion seems that practically all values are below 5 ng/ml and that 80 or 90% are below even 2 or 3 ng/ml. Clinical chemists are left to draw further conclusions but before they do so, repetition of the experiments may be useful. Two points are mentioned here, however. One is that Mertz[1] reports large geographical variation in the chromium content of several human organs. Another is that the loss of considerable amounts of chromium during storing of the sample, before the analysis, seems improbable, no decrease in chromium content being found during experiments on the same deep-frozen serum analysed at intervals during a fortnight.

Acknowledgement—The authors thank Drs. B. G. Blijenberg, Academic Hospital Rotterdam Dijkzigt for his suggestion to do this work, for discussions on the clinical aspects and for supplying some samples. Thanks are also due to the blood-transfusion service of the Sint Antonius Hospital in Utrecht for supplying the other samples.

Zusammenfassung—Ein Verfahren zur Bestimmung von Chrom in 1 ml menschlichem Blutserum oder -plasma wird beschrieben. Es beruht auf nasser Zersetzung und spektrophotometrischer Bestimmung mit Diphenylcarbazid nach Extraktion mit Isobutylmethylketon. Eine 40 mm-Küvette mit weniger als 1 ml Probenvolumen wird beschrieben.

Die Ergebnisse sind niedriger als nach Literaturangaben erwartet; die meisten Proben von gesunden Personen enthalten weniger als 2 oder 3 ng/ml. Die Reproduzierbarkeit beträgt etwa 1 ng/ml.

Résumé—On décrit une méthode pour le dosage du chrome dans 1 ml de sérum ou de plasma humain. Elle est basée sur une décomposition par voie humide et un dosage spectrophotométrique avec le diphénylcarbazide après extraction en méthylisobutylcétone. On décrit une cuvette de 40 mm avec un volume d'échantillon moindre que 1 ml. Les résultats sont plus faibles que ceux attendus de la littérature, la plupart des échantillons de personnes en bonne santé contenant moins de 2 ou 3 ng/ml. La reproductibilité est d'environ 1 ng/mil.

LITERATURE

1. W. Mertz, *Physiol. Revs.*, 1969, **49**, 163.
2. W. Niedermeier, J. H. Griggs and R. S. Johnson, *Appl. Spectry.*, 1971, **25**, 53.
3. K. Beyermann, H. J. Rose and R. P. Christian, *Anal. Chim. Acta*, 1969, **45**, 51.
4. F. J. Feldman and W. Purdy, *ibid.*, 1965, **33**, 273.
5. F. J. Feldman, E. C. Knoblock and W. Purdy, *ibid.*, 1967, **38**, 489.
6. L. C. Hansen, W. G. Scribner, T. W. Gilbert and R. E. Sievers, *Anal. Chem.*, 1971, **43**, 349.
7. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, p. 481. Springer Verlag, Berlin, 1964.
8. K. Beyermann, *Z. Anal. Chem.*, 1962, **190**, 4.
9. B. Morsches and G. Tölg, *ibid.*, 1970, **250**, 81.
10. Ref. 7, p. 73.
11. A. E. Weinhardt and A. N. Hixson, *Ind. Eng. Chem.*, 1951, **43**, 1676.
12. W. J. Youden, *Statistical Methods For Chemists*, Wiley, New York, 1951.

Talanta, 1972, Vol. 19, pp. 347 to 351. Pergamon Press. Printed in Northern Ireland

DICHLORAMINE-T AS A NEW OXIDIMETRIC TITRANT IN NON-AQUEOUS AND PARTIALLY AQUEOUS MEDIA

T. J. Jacob and C. G. R. Nair
University Department of Chemistry, Kerala University, Trivandrum-1, India

(*Received* 31 *August* 1971. *Accepted* 24 *October* 1971)

Summary—A new oxidimetric titrant, dichloramine-T, is proposed for redox titrations in glacial acetic acid medium. The general analytical conditions for using this oxidant and the procedures for potentiometric determination of ascorbic acid, iodide, arsenic(III) and iron(II) are described.

Redox titrimetry in non-aqueous media has received comparatively scant attention,[1] although considerable work has been done in acid-base titrimetry in non-aqueous media. Tomiček and co-workers carried out redox titrations in glacial acetic acid, using bromine, iodine, iodine monochloride, lead tetra-acetate, chromic acid *etc.*[2,3] Rao and Murthy used ammonium hexanitratocerate in acetonitrile as an oxidimetric reagent.[4,5,6] Our preliminary experiments indicated that a solution of dichloramine-T (*N,N'*-dichloro-*p*-toluenesulphonamide, hereafter abbreviated to DCT) in anhydrous acetic acid could be used to titrate several types of reductant. This is the first time that a metal-free organic substance has been used as an oxidimetric titrant in non-aqueous medium, as pointed out in our preliminary communication announcing this new reagent.[7] Details of individual determinations with this new oxidant are now communicated, *viz.*, potentiometric titration of ascorbic acid, iodide, arsenic(III) and iron(II).

EXPERIMENTAL

Apparatus

Smooth, clean platinum electrodes were used as indicator electrodes. A saturated calomel electrode with a potassium chloride–agar gel salt-bridge was used as reference electrode.[2–6] All titrations were done at room temperature (29 ± 2°).

Reagents

Preparation of DCT. DCT was prepared by further chlorination of chloramine-T.[8] Orton and Bradfield prepared DCT by dissolving *p*-toluenesulphonamide in acetic acid, adding bleaching powder solution, filtering off the precipitate, dissolving it in acetic acid and reprecipitating it with bleaching powder solution.[3] We found that a simpler method, passing chlorine through an aqueous solution of chloramine-T, gives good samples of DCT.

Recrystallized chloramine-T (30 g) was dissolved in water (500 ml) and pure chlorine was bubbled through the solution for about 3 hr. The fine white precipitate was filtered off, dried on the filter by sucking dry air through it and kept in a blackened vacuum desiccator for 24 hr. The sample was subsequently stored in brown bottles. The dry sample melted at 71–72° (lit.[8] 71–75°). The available chlorine was determined by dissolving an accurately weighed sample in glacial acetic acid, adding excess of 10% potassium iodide solution, diluting with water and titrating the iodine with thiosulphate solution (found 29·0%; theoretical 29·6%).

Stock solutions of DCT. Approximately 0·1*M* (∼0·4*N*) solutions were prepared by dissolving *ca.* 12 g of DCT in about 500 ml of glacial acetic acid containing 10% v/v acetic anhydride, and kept in brown or dark-painted bottles fitted with automatic burettes and guard-tubes for the exclusion of moisture. These solutions were found to be comparatively stable. The normality of a typical stock solution over a period of 15 days is given in Table I. This stability is equal or superior to the stability of other oxidimetric reagents employed in non-aqueous media.[2,3,4,5] The DCT solutions are, however, slightly decomposed by exposure to light; hence they are preserved in brown bottles. For accurate

TABLE I. STABILITY OF STOCK SOLUTIONS OF DICHLORAMINE-T IN GLACIAL ACETIC ACID, KEPT IN BROWN BOTTLES.

No. of days keeping	0	1	2	3	4	5	7	15
Normality	0·4603	0·4603	0·4603	0·4603	0·4571	0·4571	0·4571	0·4463

work, daily standardization is recommended, the method involving addition of aqueous potassium iodide solution and titrating the liberated iodine with thiosulphate.[4,5]

Determination of ascorbic acid

Standard solutions of ascorbic acid were prepared in (*a*) water, and (*b*) anhydrous acetic acid containing acetic anhydride, and standardized iodometrically.[10] Both solutions were titrated potentiometrically with DCT in glacial acetic acid. With DCT as titrant, the potential increased slightly at first; there was a sharp potential jump at the equivalence point. The attainment of equilibrium was quick. The values were found to be highly reproducible.

Reverse titrations, with ascorbic acid as titrant, give premature end-points and are therefore unsatisfactory.

Determination of potassium iodide

In view of the very low solubility of potassium iodide in glacial acetic acid and the susceptibility of iodide to aerial oxidation in presence of acid, solutions of KI in glacial acetic acid were not prepared; instead, standard aqueous solutions were used. Carbon dioxide was bubbled through the solution to exclude atmospheric oxygen during the titration. Glacial acetic acid (20 ml) and acetic anhydride (~5 ml—slightly more than the amount theoretically required to react with the water present in the KI solution) were added. The DCT solution was added from a microburette to the magnetically stirred titrand. The stirring and the carbon dioxide flow were momentarily stopped while readings were taken.

In a few titrations, 5 ml of perchloric acid were also added before the titration was started.

Determination of arsenic

Arsenious oxide was weighed out, dissolved in sodium hydroxide solution, neutralized with glacial acetic acid, and made up to standard volume with glacial acetic acid. The solution was standardized by diluting aliquots with water, adding excess of bicarbonate and titrating with standard iodine solution.

Aliquots were taken in the titration cell and slightly more than the required amounts of acetic anhydride were added. Then 20 ml of acetic acid and 5 ml of perchloric acid were added and the solution was titrated with DCT.

Determination of iron(II)

Aqueous solutions were made direct from ferrous ammonium sulphate. Glacial acetic acid solutions were prepared as follows. Solid ferrous carbonate was prepared from ferrous ammonium sulphate and sodium carbonate in aqueous solution in a carbon dioxide atmosphere. The ferrous carbonate was filtered off, washed several times with distilled water, then with alcohol and ether, and finally dried in a desiccator in an atmosphere of carbon dioxide. This ferrous carbonate was dissolved in glacial acetic acid and 5% v/v of acetic anhydride was added. Both aqueous and acetic acid ferrous solutions were standardized by permanganate titration.

Aliquots of ferrous solution were taken in the titration cell and 20 ml of glacial acetic acid were added. Preliminary experiments showed that the presence of perchloric acid is essential for the titration. Moreover, the presence of finely powdered solid potassium bromide was found to give quicker attainment of stable potentials. It was also found necessary to have phosphoric acid present to remove iron(III) by complex formation as soon as it is formed, and thereby keep the potential low till the end-point.

RESULTS AND DISCUSSION

Typical results are presented in Tables II–V. The end-points were read from the potentiometric curves, and also checked by calculations employing the Hostetter-Roberts equation.[11]

TABLE II.—POTENTIOMETRIC DETERMINATION OF ASCORBIC ACID WITH DICHLORAMINE-T

Series	Conditions	Ascorbic acid taken, *mmole*	DGT consumed, *mequiv*	Equiv. DCT per mole ascorbic acid	Error %*
(*a*)	Ascorbic acid in water	0·437$_5$	0·869	1·987	−0·6
		0·465$_4$	0·933	2·004	+0·2
		0·519$_2$	1·035	1·993	−0·3
(*b*)	Ascorbic acid	0·412$_4$	0·829	2·009	+0·5
	in glacial	0·412$_4$	0·829	2·009	+0·5
	acetic acid	0·421$_3$	0·847	2·010	+0·5

* Assuming that 2 equivalents of oxidant are consumed per mole of ascorbic acid.

TABLE III.—POTENTIOMETRIC DETERMINATION OF IODIDE WITH DICHLORAMINE-T

KI *mmole*	DCT *mequiv*	Equiv. DCT per mole KI	Error %*
0·989$_3$	0·989	1·000	0·0
0·989$_3$	0·988	0·999	−0·1
0·989$_3$	0·988	0·999	−0·1
0·989$_3$	0·988	0·999	−0·1
0·989$_3$	0·992	1·002	+0·3

* Assuming that 1 equivalent of oxidant is consumed per mole of potassium iodide.

TABLE IV.—POTENTIOMETRIC DETERMINATION OF As(III) WITH DICHLORAMINE-T

As_2O_3 taken, *mmole*	DCT consumed, *mequiv.*	Equiv. DCT per mole As_2O_3	Error %*
0·514$_0$	2·057	4·002	+0·1
0·514$_0$	2·054	3·996	−0·1
0·616$_8$	2·464	3·994	−0·1
0·616$_8$	2·469	4·002	+0·1

* Assuming that 4 equivalents of oxidant are consumed per mole of As_2O_3

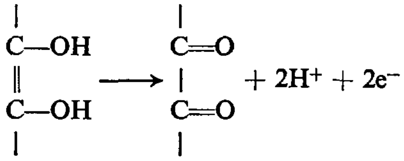
TABLE V.—POTENTIOMETRIC DETERMINATION OF Fe(II) WITH DICHLORAMINE-T

Conditions	Fe(II) taken, *mmole*	DCT consumed, *mequiv*	Equiv. DCT per mole Fe(II)	Error %*
Ferrous salt in water	0·806$_5$	0·809	1·003	+0·3
	0·806$_5$	0·809	1·003	+0·3
	0·806$_5$	0·814	1·009	+0·9
Ferrous salt in glacial acetic acid	0·995$_6$	0·994	0·998	−0·2
	0·995$_6$	0·994	0·998	−0·2
	1·245$_0$	1·243	0·998	−0·2

* Assuming that 1 equivalent of oxidant is consumed per mole of Fe(II)

Abscorbic acid

From Table II two equivalents of oxidant are consumed per mole of ascorbic acid, in agreement with the reaction



$$\begin{array}{c} | \\ \mathrm{C{-}OH} \\ \| \\ \mathrm{C{-}OH} \\ | \end{array} \longrightarrow \begin{array}{c} | \\ \mathrm{C{=}O} \\ | \\ \mathrm{C{=}O} \\ | \end{array} + 2\mathrm{H}^+ + 2e^-$$

The potential jump at the equivalence point is of the order of 600 mV for series (*a*) and 450 mV for series (*b*). The presence of water is therefore immaterial and, indeed, improves the accuracy by giving a greater potential break. Earlier workers have also remarked that small amounts of water do not cause any interference in redox titrations in non-aqueous media.[2] The lower potential break in non-aqueous medium is understandable in view of the reported inhibition of the reducing capacity of ascorbic acid in such media.[12,13]

Potassium iodide

During the titration, from the first addition of titrant, the solution becomes reddish owing to the liberation of iodine. The red colour reaches a maximum intensity and then fades to lemon yellow. Analysis of the yellow solution shows that it contains iodine in the +1 oxidation state. The fading of the red colour to lemon yellow therefore signifies the oxidation of iodine to iodine(I). Since the ICl/I couple has a standard potential $E^\circ = +1{\cdot}19$ V, it was considered desirable to raise the redox potential of the DCT/sulphonamide couple as much as possible. This potential increases with increasing acidity,[14] so perchloric acid was added.

Two breaks were observed in the titration curve. The first was sharp and corresponds to complete oxidation of iodide to iodine. The potential break was about 300 mV. Further oxidation to iodine(I) is represented by the second break (about 150 mV), which occurred much earlier than expected. This is due to loss of iodine from the solution by volatilization. In the absence of perchloric acid the second break was not satisfactory.

Arsenic

Arsenic(III) is quantitatively oxidized to arsenic(V) if perchloric acid is present; the potential break is about 50 mV.

Iron(II)

The potential break is about 200 mV for both aqueous and acetic acid solutions. As with arsenic(III) the presence of perchloric acid is necessary. This is not surprising because the Fe(III)/Fe(II) couple has a standard potential of $E^\circ = 0{\cdot}77$ V and it is advantageous to increase the potential of the DCT/sulphonamide couple by increasing the acidity. Phosphoric acid helps to give a sharper break, by complexing with the ferric iron formed. It was observed that in the absence of potassium bromide the attainment of steady potentials was slow and sluggish.

DCT

The formal redox potential of the DCT/sulphonamide couple in glacial acetic acid medium has been measured and found to be $E^\circ = 1{\cdot}2$ V.[14] This indicates that DCT is a moderately strong oxidant. The behaviour of DCT towards hydrazine, oxine, hydroquinone, and many other reductants, and back-titrations of water-insoluble organic reductants with DCT in glacial acetic acid medium are under investigation.

Zusammenfassung—Ein neues oxidimetrisches Titrationsmittel, Dichloramin-T, wird für Redoxtitrationen in Eisessig vorgeschlagen. Die allgemeinen analytischen Bedingungen zum Gebrauch dieses Oxidationsmittels und die Arbeitsvorschriften zur potentiometrischen Bestimmung von Ascorbinsäure, Jodid, Arsen(III) und Eisen(II) werden beschrieben.

Résumé—On propose un nouvel agent de titrage oxydimétrique, la dichloramine T, pour les titrages redox en milieu acide acétique glacial. On décrit les conditions analytiques générales d'emploi de cet oxydant et la technique de dosage potentiométrique de l'acide ascorbique, de l'iodure, de l'arsenic(III) et du fer(II).

REFERENCES

1. C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 822. Elsevier, London, 1960.
2. O. Tomiček and A. Heyrovský, *Collection Czech. Chem. Commun.*, 1950, **15**, 997.
3. O. Tomiček and J. Valcha, *ibid.*, 1951, **16**, 113.
4. G. P. Rao and A. R. V. Murthy, *Z. Anal. Chem.*, 1960, **177**, 86.
5. *Idem*, *ibid.*, 1961, **182**, 358; 1962, **187**, 96; 1963, **195**, 406.
6. *Idem*, *J. Phys. Chem.*, 1964, **68**, 1573.
7. T. J. Jacob and C. G. R. Nair, *Talanta*, 1965, **12**, 1055.
8. Kirk-Othmer, *Encyclopaedia of Chemical Technology*, Vol. 3, p. 671. Interscience, New York, 1954.
9. K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.* 1927, 993.
10. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, p. 626. Interscience, London, 1957.
11. J. J. Lingane, *Electroanalytical Chemistry*, p. 93. Interscience, New York, 1958.
12. L. Erdey and G. Rády, *Z. Anal. Chem.*, 1959, **166**, 127.
13. R. W. Herbert, E. L. Hirst, E. G. V. Percival, R. J. W. Reynolds and F. Smith, *J. Chem. Soc.*, 1933, 1270.
14. V. R. Nair and C. G. R. Nair, unpublished work.

Talanta, 1972, Vol. 19, pp. 353 to 359. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Determination of purity of compounds by extraction-solubility

(*Received* 16 *August* 1971. *Accepted* 29 *October* 1971)

THE USE of differential scanning calorimetry permits mole% purity of organic compounds to be determined conveniently on small samples.[1-3] The method is applicable to any organic compound which is thermally stable at its melting point, and having impurities which dissolve in the liquid phase and do not form solid solutions. If either the compound or one of its impurities is thermally unstable or if for some other reason results by differential scanning calorimetry appear to be in doubt, verification by another method is desirable. The extraction-solubility method as described by Stenger, Crummett and Kramer[4] offers an alternative. Although this approach has been reviewed by several authors[5,6,7] and in one case modified extensively by using smaller equipment, an azeotrope as a solvent, and refractive index as a measuring device in the determination of the purity of naphthalene,[8] further work showing its general applicability to the determination of the purity of compounds has not been published. Phase-solubility analysis has been reviewed by Higuchi and Conners[9] while some problems connected with this method have been studied by Wilkinson and Wragg[10]

In this paper we have applied the original technique[4] to a large number of organic compounds of high purity, tabulated the results, and made some comparisons with other methods. All results were obtained in the course of solving practical analytical problems rather than in a deliberate attempt to show the applicability of the method.

EXPERIMENTAL

In carrying out this work the method of Stenger *et al.*[4] was modified slightly. The flask and filter crucible were weighed immediately after filtering to obtain the weight when wet with solvent. (This avoids the need to wash the crystals.) Subtracting the dry weight gave the weight of solvent remaining with the crystals. When the amount of soluble impurities which remained with the crystals was high enough to affect the results, the weight was calculated from the weight of solvent and added to the amount of soluble impurities calculated to be in the residue. Other modifications and conditions are reported in the tables. The purity results in Table I were calculated as follows. "Purity from recovery" is 100 × weight recovered/sample weight. "Purity by difference" is 100—(volatiles + insolubles + solubles).

RESULTS AND CONCLUSIONS

Of the 33 compounds considered, 21 were found to be suitable for the determination of purity by extraction-solubility, 5 failed to show solubilities in the required range, and 7 were unsuitable for extraction-solubility purity determinations owing to other factors.

Successful determinations of purity are tabulated in Table I. The results compare favourably with those obtained by other methods such as infrared spectrophotometry and differential scanning calorimetry (DSC). The results are reproducible as is shown by duplicate analyses of several lots of the same compound. Also extraction-solubility was found to be an effective way to follow purification methods in several instances—piperazine hydrochloride; 4-amino-2,3,5-trichloropyridine; 3,5-dichloro-2,6-dimethyl-4-pyridinol; and 3,5-dinitro-*o*-toluamide. Surprisingly good results were obtained in some instances at low purity levels (95–99%), although the method was designed for compounds having a purity of 99·5% or better. Nine different solvents were used with equal effectiveness.

Table II lists those compounds for which no suitable solvent was found. Some solubilities are given to define the problem.

Table III identifies those compounds for which solvents showing appropriate solubilities were found but the extraction-solubility method failed owing to other difficulties. Some of these were compound decomposition, impurities more soluble in the crystals than in the solvent, formation of solid solutions, and solubility of impurity in solvent too low. Greater effort could possibly have found ways to avoid some of these difficulties, but the table serves to illustrate some of the problems associated with the practical use of the method.

Analytical Laboratories, 574 *Building*
The Dow Chemical Company
Midland, Michigan 48640, *U.S.A.*

R. A. HUMMEL
W. B. CRUMMETT

TABLE I.—COMPOUNDS TO WHICH EXTRACTION–SOLUBILITY METHOD WAS SUCCESSFULLY APPLIED

Compound	Lot	Solvent	Solubility *mg/ml*	*°C*	Extraction time, *hr*	Sample *g*	Drying conditions		Impurities, %			Purity, %		Remarks
							hr	*°C*	Volatiles	Insolubles	Solubles	From recovery	By difference	
Ethylenediaminetetra-acetic acid	A					1·4505			0·00	0·00	1·41	97·6	98·6	0·6% Chloride ions present.
	A	water	0·54	27	24	1·7767	2	90	0·00	0·00	1·78	97·7	98·2	
	B				24	1·0517			0·00	0·00	2·94	97·3	97·1	Sodium found equiv. to 2·1% mono-sodium salt.
	B				24	1·4278			0·00	0·00	2·66	97·8	97·3	Soxhlet and solubility flasks were shaken mechanically to avoid problems
2-Methyl-4-chlorophenoxy acetic acid	A	cyclohexane	0·42	24	2	1·4503	3	75	0·02	0·09	<0·02	100·0	99·89	DSC results: 99·86 (Dow) 99·84 (FDA‖)
	A	n-hexane	1·89	24	3	1·7660	3	75	0·02	0·08	0·02	99·95	99·88	
0·63% 6-Cl isomer added		n-hexane									0·81			
4-Hydroxy-3-methoxy benzaldehyde (vanillin)	A	n-hexane	1·33	25		5·0640	6	40	0·00	0·00	1·40	98·89	98·60	Difficulty encountered in removing solvent from crystals
	A					4·8755			0·00	0·00	0·96	98·46	99·04	
	B					4·7548	3	40	0·02	0·54	1·19	98·72	98·25	
	B					5·0701			0·02	0·59	0·65	99·21	98·74	
	C					4·9099		40	0·01	0·22	0·38	99·44	99·39	Sample dried to constant weight
	C					5·0501			0·01	0·20	0·39	99·53	99·40	
4,4′-Isopropylidenedi-*o*-cresol	A	cyclohexane	0·63	23	16	2·7869	1	100	0·03	0·04	0·00	99·3	99·9	
	A				16	2·9735			0·03	0·06	0·00	99·4	99·9	
N,*N*′-Diphenylethylenediamine	A	n-pentane	3·43	23	8	3·2595	1	60	0·10	1·2	3·2	95·0	95·5	Dried in vacuum oven. Solubility in n-hexane is 2·14 mg/ml but b.p. of n-hexane is higher than m.p. of the cpd.
	A				8	3·1275	1	60	0·10	1·2	3·6	94·7	95·1	
4-Hydroxyisophthalic acid	A	water	0·44	24	12	1·7950	0·5	100	0·05	0·00	1·15	99·00	98·80	Solubility increases rapidly with temperature.
	A				8	1·0422			0·03	0·06	1·16	98·89	98·75	

Compound	Lot	Solvent	Solubility		Extraction time, hr	Sample g	Drying conditions		Impurities, %			Purity, %		Remarks
			mg/ml	°*C*			*hr*	°*C*	Volatiles	Insolubles	Soluble	From recovery	By difference	
Methionine	A	methanol	0·97	23	16	2·1157	2	90	0·00	0·00	0·07	99·86	99·93	Flasks shaken 7 hr. Protected from water by drying tubes since methionine is 30x more soluble in water
	A				16	2·2511			0·00	0·00	0·11	99·94	99·89	
	B				16	1·9748			0·00	0·00	0·15	99·85	99·85	
	B				16	2·1547			0·00	0·00	0·07	99·79	99·93	
6-Chloro-2-picolinic acid	A	benzene	1·52	24	4	1·8259	2	70	0·01	0·76	0·25	99·12	98·98	
4-Amino-3,5,6-trichloro-picolinic acid (Picolam)	A	methylene chloride	0·44	23	16	2·1059	0·5	100	0·02	0·10	0·00	99·65	99·88	Tarry impurity clogged extraction thimbles. Decomposition occurred with acetonitrile
	A				16	2·073			0·02	0·07	0·00	99·75	99·91	
	B(A after 4½ yr)				9	1·0814			0·01	0·28	0·00	99·57	99·71	
4-Amino-3,5,6-trichloro-picolinic acid methyl ester	A	cyclohexane	0·46	24	4	1·3524	0·5	90	0.03	0·00	0·30	99·81	99·67	
	A				4	1·3684	0·5	90	0·03	0·00	0·20	99·84	99·77	
	B		0·41	21	3	2·1308	1	90	0·02	0·04	0·00	99·95	99·94	
					3	2·1279	1	90	0·01	0·08	0·00	99·93	99·91	
4-amino-3,5,6-trichloro-picolinic acid 2-ethylhexyl ester	A	n-hexane	4·93	24	1	1·0177	2	50	<0·02	<0·02	2.68	97·06	97·32	Dried in vacuum oven
Piperazine dihydro-chloride	A	methanol	3·41	23	8	3·8786	2	100	1·62	0·00	1·35	96·8	97·0	
	A					3·8781			1·63	0·00	1·01	97·1	97·4	
	B				8	3·3829	2	100	1·91	0·00	0·63	97·9	97·5	B is purified A. volatiles due to water.
	B					3·4841			1·90	0·00	0·63	97·2	97·5	
4-Amino-2,3,5-trichloro-pyridine	A	cyclohexane	1·01	23	4	0·7608		60	0·27	1·1	0·43	98·3	98·2	Dried to constant weight.
	A					1·0284			0·27	0·8	0·21	98·6	98·7	
	B		0·96	21	4	1·9587		60	0·00	0·02	0·15	99·78	99·83	B is purified A. Purity by DSC-99·98%. Dried to constant weight
	B		0·96	21	4	2·0795			0·00	0·05	0·14	99·78	99·81	

TABLE I (*cont*)

Compound	Lot	Solvent	Solubility *mg/ml*	°*C*	Extraction time, *hr*	Sample size, *g*	Drying conditions *hr*	Drying conditions °*C*	Impurities, % Volatiles	Impurities, % Insolubles	Impurities, % Solubles	Purity, % From recovery	Purity, % By difference	Remarks
3,5,6-Trichloro-2-pyridinol	A	n-hexane	0.58	24	3	0·7542		80	0·25	0·81	0·57	98·2	98·4	Dried to constant weight
	A				4	1·8780			0·14	0·85	0·99	97·9	98·0	
	B				4	1·9376		80	0·09	0·07	0·00	99·82	99·84	Purity by DSC-99·94%.
2,3,5-Trichloro-4-pyridinol (Pyriclor)	A	chloroform	1·77	23	5	2·0433		70	0·00	0·20	0·01	99·88	99·79	2-Pyridinol isomer remained with crystals as shown by UV 99·6% by DSC
	A					2·0154			0·00	0·19	0·01	99·83	99·80	
	A	benzene	0·62	24	4	2·0467		70	0·07	0·13	0·34	99·41	99·46	
3,5-Dichloro-2,6-dimethyl-4-pyridinol (Clopidol)	A	methanol	0·40	23	24	2·2479	1	100	0·02	0·00	0·11	99·90	99·87	
	A					2·3323			0·02	0·00	0·06	99·85	99·92	
	B				30	1·1962			0·02	0·1	0·60	99·20	99·3	
	B					1·3661			0·02	0·0	0·63	99·33	99·4	
	C				8	1·1257			0·06	0·0	2·34	97·46	97·60	
	C					1·1497			0·03	0·0	2·36	97·35	97·61	
	D				12	1·8608			0·00	0·04	0·53	99·52	99·43	Recrystallized C
2,6-Dimethyl-4-pyridinol	A	acetone	0·51	24	3	0·9558	6	50	1·47	0·15	0·09	98·5	98·29	Dried in vacuum oven
	A					0·9712			1·47	0·20	0·16	98·5	98·17	Volatiles due to water
3-Hydroxy-2-methyl-4-pyrone (Maltol)	A	n-hexane	0·23	23	3	0·9794		50	0·05	0·00	0·22	99·93	99·73	Dried to constant weight
	A					1·1564			0·03	0·00	0·16	99·84	99·81	
	B					1·1365			0·00	0·00	0·29	99·74	99·71	
	B					1·0866			0·01	0·00	0·32	99·69	99·67	
4,4′-Cyclohexylidene bis (2-cyclohexy phenol)	A	cyclohexane	1·36	23	8	2·3913	2	110	0·01	0·00	0·00	99·7	99·99	
	A					2·6503			0·01	0·02	0·00	99·9	99·97	
3,5-dinitro-*o*-toluamide (Zoalene)	A	water	0·76	24	16	3·8007	1	100	0·05	0·11	2·4	97·6	97·4	Some decomposition on heating in water
	A					3·9095			0·05	0·4	1·0	98·9	98·5	
	A	benzene	0·50	24	8	4·0096			0·03	0·43	0·32	99·2	99·2	
	A					3·9526			0·39	0·39	0·35	98·8	99·2	IR assay 98·7%

Compound	Lot	Solvent	Solubility mg/ml	°C	Extraction time, hr	Sample g	Drying conditions hr	°C	Impurities, % Volatiles	Insolubles	Solubles	Purity, % From recovery	By difference	Remarks
	B		0·61	25	4	2·1821			0·03	0·32	0·34	99·30	99·31	
	B					2·2330			0·04	0·26	0·30	99·26	99·40	
	C					2·4110			0·01	0·40	0·39	99·15	99·20	75% Acetone slurry-wash of B.
	C					2·4517			0·03	0·38	0·43	99·17	99·16	
	D					2·6578			0·00	0·04	0·00	99·95	99·96	B recrystallized from 75% acetone.
	D					2·5606			0·00	0·06	0·09	99·94	99·85	
	E					2·3409			0·00	0·14	0·00	99·98	99·86	B recrystallized from 2B ethanol.
	E					2·3480			0·00	0·09	0·03	99·95	99·88	
	F					2·8818			0·00	0·01	0·00	99·94	99·99	Recrystallized E.
	G		0·61	24		2·0613			0·03	0·04	0·00	100·2	99·93	B recrystallized from 1-methoxy-2-propanol.
	G					2·0143			0·02	0·03	0·00	100·2	99·95	
Trifluoroacetyl urea	A	benzene	1·41	24	3	0·5659	2	24	0·23	0·55	0·55	98·75	98·67	Dried in vacuum oven. 98·8% by alkaline hydrolysis (corrected for 0·43% free acid). Some volatility with benzene.

TABLE II.—COMPOUNDS FOR WHICH A SUITABLE SOLVENT COULD NOT BE FOUND (EXTRACTION-SOLUBILITY METHOD INAPPLICABLE)

Compound	Observations
3,5-Dichloro-4-methoxy-2,6-lutidine	Solubility > 10 mg/ml of acetone, benzene, carbon disulphide, carbon tetrachloride, chloroform, cyclohexane, or n-hexane; 140 mg/ml of methanol; 0·1 mg/ml of water at 23°C.
Phosphoric acid, diethyl-(3,5,6-trichloro-2-pyridyl) ester	Solubility too high in organic solvents—100 mg/ml of iso-octane, 180 mg/ml of n-hexane at 23°C. Solubility in water 0·5 mg/ml is in range but compound hydrolyses in water.
Phosphorothioic acid, *O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl) ester	Solubility in n-hexane 89 mg/ml at 0°C. Other hydrocarbons and methanol about the same. Other organic solvents greater amounts. Solubility in water 0·0004 mg/ml at 24°C.
Phosphorothioic acid, *O*,*O*-dimethyl-*O*-(3,5,6-trichloro-2-pyridyl) ester	Lowest solubility in an organic solvent was 160 mg/ml in n-hexane at 23°C (0·004 mg/ml in water).
4,4′-(2,3-dimethyltetramethylene)dipyrocatechol (nordihydroguaiaretic acid)	Solubility too low except in alcohols and ether, in which it is too high.

TABLE III.—COMPOUNDS FOR WHICH SOLUBILITY SUITABLE BUT RESULTS UNSATISFACTORY

Compound	Solvent	Solubility *mg/ml*	*°C*	Observations
2,4,5-Trichlorophenoxyacetic acid	carbon tetrachloride	0·48	23	Methoxy impurity not detected.
	benzene	2·2	23	Methoxy impurity not detected.
Methylcarbamic acid, 4-dimethylamino-3,5-xylyl ester	water	0·1	25	Decomposed on extraction with water. Solubility in other solvents too high.
Dehydroacetic acid (3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione)	n-hexane	2·9	23	No difference in total weight of soluble impurities between 1-g and 2-g samples although these were detected by TLC.
4-Amino-3,5-dichloro-2,6-lutidine	n-hexane	1·8	23	Impurities concentrated on the recrystalized material.
5-Chloro-4-hydroxy-2,6-dimethylnicotinic acid	acetone	0·25	23	2, 6-Dimethyl-4-hydroxynicotinic acid impurity not in soluble impurities although shown to be present by ion-exchange–UV method.
N, *N*′-Dimethylphosphorodiamidic acid, 4-t-butyl-2-chlorophenyl ester	n-hexane	0·44	23	0·3% Soluble impurities found. By GLC 0·9% unchlorinated phenyl ester found. Purity by DSC 99·4%
Tricyclohexylhydroxystannane	n-hexane	0·20	25	Compound decomposed, losing water during extraction

Summary—Thirty-three organic compounds prepared for use as analytical standards were examined for purity by the extraction-solubility method. Of these, twenty-one gave satisfactory results, seven behaved non-ideally, and five were not soluble in the useful range. Results on the twenty-one satisfactory samples compared favourably with those obtained by differential scanning calorimetry and other analytical methods. The method was found to be useful for following the improvement of compounds undergoing purification.

Zusammenfassung—Dreiunddreißig zur Verwendung als analytische Standards hergestellte organische Verbindungen wurden mit der Extraktions-Löslichkeitsmethode auf Reinheit untersucht. Darunter gaben einundzwanzig befriedigende Ergebnisse, sieben verhielten sich nicht ideal, und fünf waren im nutzbaren Bereich nicht löslich. Die Ergebnisse von den einundzwanzig zufriedenstellenden Proben schneiden beim Vergleich mit solchen von Untersuchungen mit registrierender Differentialkalorimetrie und anderen analytischen Methoden gut ab. Die Methode wurde zur Kontrolle der Verbesserung von Verbindungen während des Reinigungsprozesses für nützlich befunden.

Résumé—On a examiné la pureté de trente trois composés organiques préparés pour l'emploi comme étalons analytiques par la méthode d'extraction-solubilité. De ceux-ci, vingt et un donnent des résultats satisfaisants, sept se comportent de maniére non idéale, et cinq ne sont pas solubles dans le domaine utile. Les résultats obtenus avec les vingt et un échantillons satisfaisants sont favorablement comparables à ceux obtenus par l'analyse enthalpique différentielle et d'autres méthodes analytiques. On a trouvé que la méthode est utile pour suivre l'amélioration de composés soumis à purification.

REFERENCES

1. N. J. DeAngelis and G. J. Papariello, *J. Pharm. Sci.*, 1968 **57**, 1868.
2. C. Plato and A. R. Glasgow, Jr., *Anal. Chem.*, 1969 **41**, 330.
3. R. Reubke and J. A. Mollica, *J. Pharm. Sci.*, 1967 **56**, 822.
4. V. A. Stenger, W. B. Crummett and W. R. Kramer, *Anal. Chem.*, 1953 **25**, 974.
5. W. J. Mader, *Organic Analysis*, Vol. 2, Interscience, New York, 1954, p 253.
6. *Idem*, *C.R.C. Critical Reviews in Anal. Chem.*, 1970, **1**, 193.
7. V. A. Stenger, W. B. Crummett and J. G. Cobler, *Chemical Analysis of Resin-Based Coating Materials*, C.P.A. Kappelmeier, ed., Interscience, New York, 1959, p 587.
8. R. Friedenberg and P. J. Januke, *Anal. Chim. Acta*, 1965 **31**, 655.
9. T. Higuchi and K. A. Conners, *Advances in Analytical Chemistry and Instrumentation*, Vol. 4, p. 117. C. N. Reilley, ed., Interscience, New York, 1965.
10. J. V. Wilkinson and J. S. Wragg, *Analyst*, 1966, **91**, 600.
11. Food and Drug Administration Primary Standard Data Sheet No. 85. June 1968. Dept. Health, Educ. and Welfare, Washington, D.C.

Talanta, 1972, Vol. 19, pp. 359 to 363. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in lubricating oils by cool-flame emission spectroscopy

(*Received* 2 *August* 1971. *Accepted* 14 *October* 1971)

An analytical procedure, based on the cool-flame technique of Dagnall *et al.*,[1] has been developed for the determination of phosphorus in lubricating oils; phosphorus is commonly present in these oils in the form of the additive zinc dialkyldithiophosphate and the present method forms an alternative to procedures published elsewhere[2] for this determination.

Brite[3] and Davis *et al.*[4] have shown that phosphorus in organophosphorus compounds may be detected by measurement at 540 nm of the flame emission continuum produced when solutions of the material in various organic solvents are aspirated into an oxy-hydrogen flame. In our experience, it is difficult to obtain specific and quantitative measurements under these conditions and a more certain indication of phosphorus is obtained by using the emission from the HPO species at 528 nm, produced when aqueous solutions containing phosphorus are aspirated into a cool hydrogen–nitrogen

range. Results on the twenty-one satisfactory samples compared favourably with those obtained by differential scanning calorimetry and other analytical methods. The method was found to be useful for following the improvement of compounds undergoing purification.

Zusammenfassung—Dreiunddreißig zur Verwendung als analytische Standards hergestellte organische Verbindungen wurden mit der Extraktions-Löslichkeitsmethode auf Reinheit untersucht. Darunter gaben einundzwanzig befriedigende Ergebnisse, sieben verhielten sich nicht ideal, und fünf waren im nutzbaren Bereich nicht löslich. Die Ergebnisse von den einundzwanzig zufriedenstellenden Proben schneiden beim Vergleich mit solchen von Untersuchungen mit registrierender Differentialkalorimetrie und anderen analytischen Methoden gut ab. Die Methode wurde zur Kontrolle der Verbesserung von Verbindungen während des Reinigungsprozesses für nützlich befunden.

Résumé—On a examiné la pureté de trente trois composés organiques préparés pour l'emploi comme étalons analytiques par la méthode d'extraction-solubilité. De ceux-ci, vingt et un donnent des résultats satisfaisants, sept se comportent de manière non idéale, et cinq ne sont pas solubles dans le domaine utile. Les résultats obtenus avec les vingt et un échantillons satisfaisants sont favorablement comparables à ceux obtenus par l'analyse enthalpique différentielle et d'autres méthodes analytiques. On a trouvé que la méthode est utile pour suivre l'amélioration de composés soumis à purification.

REFERENCES

1. N. J. DeAngelis and G. J. Papariello, *J. Pharm. Sci.*, 1968 **57**, 1868.
2. C. Plato and A. R. Glasgow, Jr., *Anal. Chem.*, 1969 **41**, 330.
3. R. Reubke and J. A. Mollica, *J. Pharm. Sci.*, 1967 **56**, 822.
4. V. A. Stenger, W. B. Crummett and W. R. Kramer, *Anal. Chem.*, 1953 **25**, 974.
5. W. J. Mader, *Organic Analysis*, Vol. 2, Interscience, New York, 1954, p 253.
6. *Idem*, *C.R.C. Critical Reviews in Anal. Chem.*, 1970, **1**, 193.
7. V. A. Stenger, W. B. Crummett and J. G. Cobler, *Chemical Analysis of Resin-Based Coating Materials*, C.P.A. Kappelmeier, ed., Interscience, New York, 1959, p 587.
8. R. Friedenberg and P. J. Januke, *Anal. Chim. Acta*, 1965 **31**, 655.
9. T. Higuchi and K. A. Conners, *Advances in Analytical Chemistry and Instrumentation*, Vol. 4, p. 117. C. N. Reilley, ed., Interscience, New York, 1965.
10. J. V. Wilkinson and J. S. Wragg, *Analyst*, 1966, **91**, 600.
11. Food and Drug Administration Primary Standard Data Sheet No. 85. June 1968. Dept. Health, Educ. and Welfare, Washington, D.C.

Talanta, 1972, Vol. 19, pp. 359 to 363. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in lubricating oils by cool-flame emission spectroscopy

(*Received* 2 *August* 1971. *Accepted* 14 *October* 1971)

AN ANALYTICAL PROCEDURE, based on the cool-flame technique of Dagnall *et al.*,[1] has been developed for the determination of phosphorus in lubricating oils; phosphorus is commonly present in these oils in the form of the additive zinc dialkyldithiophosphate and the present method forms an alternative to procedures published elsewhere[2] for this determination.

Brite[3] and Davis *et al.*[4] have shown that phosphorus in organophosphorus compounds may be detected by measurement at 540 nm of the flame emission continuum produced when solutions of the material in various organic solvents are aspirated into an oxy-hydrogen flame. In our experience, it is difficult to obtain specific and quantitative measurements under these conditions and a more certain indication of phosphorus is obtained by using the emission from the HPO species at 528 nm, produced when aqueous solutions containing phosphorus are aspirated into a cool hydrogen–nitrogen diffusion flame.[1] Since, as reported by Aldous *et al.*,[5] the HPO emission in the cool flame is completely quenched by the introduction of organic liquids, it is impracticable to work directly with a solution of the oil sample in an organic solvent; the only strong emission we have observed with certainty under these conditions can be attributed to the C_2 band at 516 nm.

Investigation of possible chemical pretreatments of the oil, to provide an aqueous solution suitable for cool-flame analysis, indicated that severe interference effects were present in solutions prepared by either the wet-oxidation process of IP 148/58[2] or the zinc oxide ashing technique of IP 149/58;[2] high residual contents of mineral acid or of bivalent cations are not readily removed. A new pretreatment was devised, in which the oil was ashed in the presence of potassium hydroxide; the residual melt was dissolved in water and treated with cation-exchange resin, and the phosphorus content of the final solution was measured, using the general procedure described in other published applications.[6,7]

EXPERIMENTAL

Reagents

Potassium hydroxide. Pellets, analytical reagent grade.

Orthophosphoric acid. Analytical reagent grade was used to prepare the reference standard. An accurate 0·001*M* solution, containing 31 μg of P/ml, was prepared by dilution of a standardized stock solution.

Dowex 50W-X8 *cation-exchange resin.* A resin bed 0·25 m long and 20 mm in diameter was found satisfactory for 3 sample treatments. Resin stocks were regenerated by stirring for 8 hr with 0·3*M* hydrochloric acid, followed by decantation and washing until acid-free.

Apparatus

Unicam SP 900 flame photometer, fitted with standard 13-hole air–propane burner head, or with an open Pyrex glass tube, 10 mm bore, attached by a short polythene sleeve to a standard burner shaft. In both cases, the burner head was sited 10 mm below the bottom of the monochromator entrance slit. Nitrogen, at 105 kN/m^2 (15 psi) (2·5 l./min), was fed through the SP 900 nebulizing system and hydrogen, at 20 mm pressure on the dibutyl phthalate manometer (1·2 l./min), was fed through the fuel system. The solution uptake rate was 2·5 ml/min. Other instrument settings were: slitwidth 0.35 mm; electrical bandwidth 3; gain control 4–5, as necessary.

Procedure

Transfer 1 ± 0·005 g of oil to a small nickel or platinum crucible and add 0·5 g of potassium hydroxide pellets. Heat gently over a low flame until the potassium hydroxide melts and the oil ignites. Continue heating until the oil has burned off, then ignite more strongly until a clean white residue is obtained, taking care to avoid loss by spitting. Cool, add 10 ml of water and transfer the dissolved melt, with washings, to a 100-ml beaker. Add 5 g of wet resin and stir mechanically for 10 min or until the solution loses all turbidity. Transfer to the resin column and collect the effluent in a 250-ml graduated flask. Wash with successive 25-ml portions of water, at a flow-rate of 10 ml/min, to a final total volume of 250 ml.

Measure, by pipette, two 50-ml aliquots of this solution into two 100-ml graduated flasks and to one aliquot add a suitable volume (*V* ml) of the standard phosphorus solution (Note 1). Dilute both solutions to volume.

Measure the emission at the peak response wavelength (approx. 528 nm) for both solutions alternately, and record the mean galvanometer deflections for each from at least 3 replicate readings. (Note 2). Spray distilled water after each pair of readings to restore the galvanometer to zero. Any blank determination required should be carried out by the same procedure (Note 3).

From the mean readings for the sample (S_0) and the sample with added phosphorus (S_1), calculate the phosphorus content of the sample from the expression:

$$\% \mathrm{P} = \frac{(S_0) \times V \times 31 \times 250 \times 100 \times 100}{(S_1 - S_0) \times \text{weight of oil (g)} \times 10^6 \times 50 \times 100}$$

For a fixed sample weight of 1 g this reduces to:

$$\% \mathrm{P} = \frac{(S_0)}{(S_1 - S_0)} \times V \times 0{\cdot}0155$$

Notes. 1. Ascertain the approximate phosphorus content of the sample solution by spraying the first 50-ml aliquot—diluted to volume—and, with the SP 900 settings unaltered, spray a series of standards to determine the concentration giving about the same response. The volume (*V* ml) to be added to the second 50-ml aliquot can then be estimated, and should make $S_0/(S_1 - S_0)$ approximately unity.[8]

2. Adjust the gain control, on a trial spraying, so that the phosphorus-doped aliquot gives a galvanometer deflection of about 80–90% full scale.

3. Blank determinations on the reagents, including potassium hydroxide, have not shown any measurable response. If it is desired to measure any blank contribution by the base oil, as distinct from the phosphorus-containing additive, ash 1 g of base oil in the same way as for the sample and apply the result as a correction to the total phosphorus result. Provided that fresh resin is used, this correction has not been found to exceed 0·002% P, but high and variable blanks may be obtained if the resin is not fresh.

RESULTS AND DISCUSSION

The method was tested on a series of synthetic oil blends prepared in the laboratory, on a weight/weight basis, from OMD 370 base oil and analysed oil additives. The compositions of the blends and the phosphorus contents found are listed in Table I; these results were obtained at various intervals over a period of 5–6 weeks.

Since the procedure measures total phosphorus in the oil, a separate determination was run on the base oil, so that the added phosphorus could be obtained by difference and it was the application of this correction that revealed, in the early stages of the work, that high and variable blanks were likely to be recorded unless fresh resin was used and adequate stirring given in the initial treatment. Once this point was established, blank corrections dropped from a level of about 0·008–013% P to a steady figure of about 0·002% and this latter correction was applied to the results given in Table I. In fact, there was no evidence that the blank signal was actually due to phosphorus; spectral scans on solutions concentrated from larger (5 g) samples of base oil did not show the three characteristic HPO peaks at 512, 528 and 560 nm and the correction could therefore be regarded as a background compensation.

There was no indication that the phosphorus results shown in Table I were subject to interference by the other metals—calcium, barium and zinc—present in the oil additives.

TABLE I.—ANALYSIS OF SYNTHETIC OIL BLENDS

Blend	No. of Replicates	% *w/w*				
		Added				Found
		Ca	Ba	Zn	P	P
A.1	4	—	—	0·025	0·022	0·022
A.2	4	—	—	0·068	0·059	0·057
A.3	6	—	—	0·123	0·107	0·106
B.1	6	—	0·219	—	0·009	0·009
B.2	4	—	0·413	—	0·017	0·018
B.3	5	—	0·716	—	0·080	0·078
C.1	3	—	0·60	0·10	0·094	0·096
C.2	5	—	0·60	0·14	0·132	0·130
C.3	4	—	0·60	0·04	0·038	0·037
D.1	5	—	0·40	0·10	0·094	0·098
D.2	6	—	0·40	0·14	0·132	0·137
D.3	4	—	0·40	0·04	0·038	0·037
E.1	5	—	0·20	0·10	0·094	0·096
E.2	4	—	0·20	0·14	0·132	0·137
E.3	4	—	0·20	0·04	0·038	0·032
F.1	4	0·054	—	—	0·030	0·029
F.2	3	0·325	—	—	0·145	0·147

A further series of analyses was made on 8 samples available through the Institute of Petroleum Atomic Absorption Sub-Panel ST-G-4E. The results, given in Table II, are shown in comparison with the nominal phosphorus contents; eventually, analytical results obtained by a range of techniques will become available on these oil blends.

In a separate precision test, 10 replicate analyses were performed on blend C.3 (Table I); the mean result was 0·039% P, with a coefficient of variation of ±5%.

TABLE II.—ANALYSIS OF I.P. OIL BLENDS

Blend	No. of Replicates	% w/w				
		Nominal				Found
		Ca	Ba	Zn	P	P
1	6	0·5	0·4	0·2	0·2	0·20
2	6	1·5	0·2	0·8	0·08	0·076
3	6	2·2	0·6	0·05	0·05	0·042
4	6	0·2	0·17	0·15	0·05	0·053
5	6	0·05	0·04	0·12	0·12	0·10
6	6	0·12	0·95	0·08	0·08	0·068
7	4	0·10	0·08	0·07	0·14	0·16
8	4	0·02	0·12	0·03	0·03	0·026

CONCLUSIONS

The cool-flame technique provides a rapid alternative to the standard chemical methods[2] for the determination of phosphorus in lubricating oils. A single determination can be completed in approximately 2½ hr and for a batch of 8 samples the time is reduced to approximately 1 hr per sample. The precision is acceptable in terms of the repeatability and reproducibility criteria laid down in the alternative methods,[2] and the accuracy is satisfactory as measured by the results shown in Table I, which indicate an average deviation of 0·0025% P from the true result.

Quality Assurance Directorate (Materials)
Royal Arsenal
*London, S.E.*18

W. N. ELLIOTT
C. HEATHCOTE
R. A. MOSTYN

Summary—The phosphorus content of lubricating oils is determined by measurement of the emission from the HPO molecular species at 528 nm in a cool hydrogen–nitrogen diffusion flame. The oil is ashed in the presence of potassium hydroxide and an aqueous extract of the melt is treated with ion-exchange resin to remove interferents, before aspiration into the flame. Analytical results are presented on samples containing phosphorus in the range 0·009–0·2%. The precision of the method is ±5% at the 0·04% phosphorus level.

Zusammenfassung—Der Phosphorgehalt von Schmierölen wird durch Messung der Emission des HPO-Moleküls bei 528 nm in einer kühlen Wasserstoff-Stickstoff-Diffusionsflamme bestimmt. Das Öl wird in Gegenwart von Kaliumhydroxid verascht und ein wäßriger Extrakt der Schmelze mit Ionenaustauschharz behandelt, um vor dem Ansaugen in die Flamme störende Bestandteile zu entfernen. Analysenergebnisse von Proben mit Phosphorgehalten im Bereich 0·009–0·2% werden angegeben. Die Genauigkeit der Methode beträgt ±5% bei 0·04% Phosphorgehalt.

Résumé—On dose la teneur en phosphore d'huiles de lubrification par mesure de l'émission de l'espèce moléculaire HPO à 528 nm dans une flamme de diffusion hydrogène-azote froide. L'huile est incinérée en la présence de potasse et l'on traite un extrait aqueux de la masse fondue par une résine échangeuse d'ions pour éliminer les substances gênantes, avant aspiration dans la flamme. On présente les résultats analytiques pour des échantillons contenant 0,009–0,2% de phosphore. La précision de la méthode est de ±5% pour une teneur en phosphore de 0,04%.

REFERENCES

1. R. M. Dagnall, K. C. Thompson and T. S. West, *Analyst*, 1968, **93**, 72.
2. *Institute of Petroleum Standards*, 27th Ed., Part 1, Section 2, Methods IP 148/58 and IP 149/58, Institute of Petroleum, London, 1968.

3. D. W. Brite, *Anal. Chem.*, 1955, **27**, 1815.
4. A. Davis, F. J. Dinan, E. J. Lobbett, J. D. Chazin and L. E. Tufts, *ibid.*, 1964, **36**, 1066.
5. K M. Aldous, R. M. Dagnall and T. S. West, *Analyst*, 1970, **95**, 417.
6. W. N. Elliott and R. A. Mostyn, *J. Oil Col. Chem. Assoc.*, 1970, **53**, 989.
7. *Idem*, *Analyst*, 1971, **96**, 452.
8. T. E. Beukelman and S. S. Lord, *Appl. Spectry.*, 1960, **14**, 12.

Talanta, 1972, Vol. 19, pp. 363 to 366. Pergamon Press. Printed in Northern Ireland

Neutron-activation analysis for thorium in zircon

(*Received* 26 *July* 1971. *Accepted* 19 *October* 1971)

NEUTRON-ACTIVATION analysis is a sensitive method for the determination of traces of thorium in geological specimens.[1-5] It is, therefore, surprising that the technique has not been applied for the determination of this element in zircon, although this analysis is of great geochemical interest.[6-8] Recently Mantel and co-workers,[9] Gordon *et al.*[10] and Meyer[11] have reported non-destructive neutron-activation determination of thorium in silicate rock samples, using Ge(Li) detectors. When attempts were made to analyse zircon samples for thorium by using a 3 ml Ge(Li) detector, the 299 and 311 keV gamma-rays of ^{233}Pa were barely identifiable over the high intensity Compton continuum from the prominent gamma-rays of ^{181}Hf. Hence it was not investigated further.

Preliminary experiments revealed that the radiochemical methods reported in the literature, based on ion-exchange separations of ^{233}Pa[5,12,13] or solvent extraction with *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA),[14] when applied to zircons, did not give radiochemically pure ^{233}Pa. It was particularly difficult to remove ^{95}Nb, ^{182}Ta and ^{181}Hf produced in significant amounts on irradiation of zircons.[15]

Sill[16] has separated ^{233}Pa on barium sulphate. This procedure was applied in the present study and its adequacy for giving radiochemically pure ^{233}Pa was evaluated by the analysis of U.S.G.S. standard rock samples and then applied for the analysis of a number of zircons.

EXPERIMENTAL

Apparatus

Gamma-ray spectra were taken with a 400-channel analyser coupled to a 75 × 75 mm NaI(Tl) detector system.

Reagents

Thorium standard. Thorium dioxide (1·138 g) was dissolved by boiling with 50 ml of nitric acid (1 + 1). A few drops of 2% hydrofluoric acid were occasionally added to facilitate the dissolution. After repeated evaporation with nitric acid to remove residual fluoride, the solution was made up to 100 ml. The solution was further diluted to give a standard solution containing 100 μg of Th/ml.

Manganese carrier. Potassium permanganate (2·87 g) was dissolved in nitric acid (1 + 20), 2 or 3 drops of 30% hydrogen peroxide were added, the solution was boiled to remove excess of hydrogen peroxide, and diluted to give a solution containing 10 mg of Mn/ml.

Barium carrier. Barium chloride dihydrate (6·6 g) was dissolved in 100 ml of distilled water.

Zirconium carrier. Hydrated zirconyl nitrate (3·66 g) was heated with 5–10 ml of concentrated sulphuric acid, cooled and made up to 100 ml to give a solution containing 5 mg of Zr/ml.

Irradiation of samples

Samples were wrapped in high-purity aluminium foil. Thorium standard solution (100 μl) was evaporated on a small piece of aluminium foil and then wrapped in a second foil. The sample and standard were sealed in an aluminium can and irradiated for 2–3 days in the CIRUS reactor (natural uranium, heavy-water moderated reactor of the NRX type) at a flux of 3×10^{10} n.mm^{-2}.sec^{-1} and then cooled for a week.

Chemical procedure

Evaporate 1 ml of the barium carrier solution in a nickel crucible. Transfer 50–100 mg of irradiated sample, weighed to ±0·2 mg, to the crucible. Fuse with 1–2 g of sodium peroxide. Cool the fused mass and leach it with water in a 100-ml beaker, wash the crucible with water and with

3. D. W. Brite, *Anal. Chem.*, 1955, **27**, 1815.
4. A. Davis, F. J. Dinan, E. J. Lobbett, J. D. Chazin and L. E. Tufts, *ibid.*, 1964, **36**, 1066.
5. K M. Aldous, R. M. Dagnall and T. S. West, *Analyst*, 1970, **95**, 417.
6. W. N. Elliott and R. A. Mostyn, *J. Oil Col. Chem. Assoc.*, 1970, **53**, 989.
7. *Idem*, *Analyst*, 1971, **96**, 452.
8. T. E. Beukelman and S. S. Lord, *Appl. Spectry.*, 1960, **14**, 12.

Talanta, 1972, Vol. 19, pp. 363 to 366. Pergamon Press. Printed in Northern Ireland

Neutron-activation analysis for thorium in zircon

(*Received* 26 *July* 1971. *Accepted* 19 *October* 1971)

NEUTRON-ACTIVATION analysis is a sensitive method for the determination of traces of thorium in geological specimens.[1–5] It is, therefore, surprising that the technique has not been applied for the determination of this element in zircon, although this analysis is of great geochemical interest.[6–8] Recently Mantel and co-workers,[9] Gordon *et al.*[10] and Meyer[11] have reported non-destructive neutron-activation determination of thorium in silicate rock samples, using Ge(Li) detectors. When attempts were made to analyse zircon samples for thorium by using a 3 ml Ge(Li) detector, the 299 and 311 keV gamma-rays of ^{233}Pa were barely identifiable over the high intensity Compton continuum from the prominent gamma-rays of ^{181}Hf. Hence it was not investigated further.

Preliminary experiments revealed that the radiochemical methods reported in the literature, based on ion-exchange separations of ^{233}Pa[5,12,13] or solvent extraction with *N*-benzoyl-*N*-phenylhydroxylamine (NBPHA),[14] when applied to zircons, did not give radiochemically pure ^{233}Pa. It was particularly difficult to remove ^{95}Nb, ^{182}Ta and ^{181}Hf produced in significant amounts on irradiation of zircons.[15]

Sill[16] has separated ^{233}Pa on barium sulphate. This procedure was applied in the present study and its adequacy for giving radiochemically pure ^{233}Pa was evaluated by the analysis of U.S.G.S. standard rock samples and then applied for the analysis of a number of zircons.

EXPERIMENTAL

Apparatus

Gamma-ray spectra were taken with a 400-channel analyser coupled to a 75 × 75 mm NaI(Tl) detector system.

Reagents

Thorium standard. Thorium dioxide (1·138 g) was dissolved by boiling with 50 ml of nitric acid (1 + 1). A few drops of 2% hydrofluoric acid were occasionally added to facilitate the dissolution. After repeated evaporation with nitric acid to remove residual fluoride, the solution was made up to 100 ml. The solution was further diluted to give a standard solution containing 100 μg of Th/ml.

Manganese carrier. Potassium permanganate (2·87 g) was dissolved in nitric acid (1 + 20), 2 or 3 drops of 30% hydrogen peroxide were added, the solution was boiled to remove excess of hydrogen peroxide, and diluted to give a solution containing 10 mg of Mn/ml.

Barium carrier. Barium chloride dihydrate (6·6 g) was dissolved in 100 ml of distilled water.

Zirconium carrier. Hydrated zirconyl nitrate (3·66 g) was heated with 5–10 ml of concentrated sulphuric acid, cooled and made up to 100 ml to give a solution containing 5 mg of Zr/ml.

Irradiation of samples

Samples were wrapped in high-purity aluminium foil. Thorium standard solution (100 μl) was evaporated on a small piece of aluminium foil and then wrapped in a second foil. The sample and standard were sealed in an aluminium can and irradiated for 2–3 days in the CIRUS reactor (natural uranium, heavy-water moderated reactor of the NRX type) at a flux of 3×10^{10} n.mm^{-2}.sec^{-1} and then cooled for a week.

Chemical procedure

Evaporate 1 ml of the barium carrier solution in a nickel crucible. Transfer 50–100 mg of irradiated sample, weighed to ±0·2 mg, to the crucible. Fuse with 1–2 g of sodium peroxide. Cool the fused mass and leach it with water in a 100-ml beaker, wash the crucible with water and with nitric acid (1 + 1). Acidify the solution carefully with nitric acid. If silica separates, centrifuge and separate the residue. Transfer the residue to a platinum dish and volatilize the silica with a hydrofluoric–nitric acid mixture. Remove the fluorides by repeated evaporation with nitric acid. Dissolve the residue in nitric acid (1 + 1) and transfer to the main solution. Add 20 mg of manganese carrier to the solution and heat on a water-bath. Add about 2 g of solid potassium bromate to precipitate manganese dioxide. Boil, centrifuge and reject the supernatant liquid. Transfer the precipitate to a beaker and dissolve the manganese dioxide with nitric acid (1 + 1) and 2 or 3 drops of dilute hydrogen peroxide. Boil the solution and reprecipitate the manganese dioxide. Dissolve the precipitate in nitric acid (1 + 1) and a few drops of dilute hydrogen peroxide, add 1 ml of the barium solution, and 7 ml of concentrated sulphuric acid. Heat the solution on a hot-plate to fumes of sulphur trioxide. Cool and add 25–30 ml of water to precipitate barium sulphate. Boil the solution for 5 min, cool, centrifuge and reject the supernatant. Slurry the barium sulphate with water and transfer to the same beaker, wash the centrifuge tube with 7 ml of sulphuric acid and add the washings to the beaker. Evaporate the solution on a hot-plate to fumes of sulphur trioxide. Cool the solution to 50–70°, add 150–200 mg of potassium dichromate to oxidize ^{239}Np, and heat the beaker on a boiling water-bath for 5 min. Cool to about 50°, dilute to 40–50 ml with water, boil for 5 min. Filter the solution through a demountable filtering unit containing a small circle of Whatman No. 42 filter paper. Take out the filter circle, with the precipitate, dry it and mount it on an aluminium card, and count the activity of ^{233}Pa under the 310 keV photopeak. Check the decay curve.

Dissolve with dilute hydrochloric acid the aluminium foil containing the thorium standard and evaporate to dryness. Dissolve the residue in 10 ml of nitric acid (1 + 1) and dilute the solution to a known volume. Treat a suitable aliquot as described above.

RESULTS AND DISCUSSION

The hydrolytic nature of protactinium and the non-availability of suitable carriers have led many earlier workers to employ ^{231}Pa for evaluating the yield of ^{233}Pa in radiochemical methods.[4,17,18] Others[5,19–23] established that high and nearly constant yields are obtained in their procedures before the analysis of samples by these methods. The results of Sill[16] and the preliminary studies made in the present work indicated the nearly quantitative recovery of ^{233}Pa during its co-precipitation on barium sulphate. The method was, therefore, applied to the determination of Th in U.S.G.S. standard samples. The results given in Table I indicate the adequacy of the method. However, it was felt desirable to establish that similar recoveries were obtained in the analysis of matrices such as zircon. Hence one portion of the irradiated zircon was spiked with a known amount of the thorium standard and the thorium content computed by the standard addition technique. This value was comparable with that obtained by direct comparison of the activities from the sample and the

Table I.—Thorium content of U.S.G.S. standard rock samples

Author	Technique	AGV-1 *ppm*	BCR-1 *ppm*	G-2 *ppm*	GSP-1 *ppm*
Present work	R.A.A.	7·3	6·7	30	115
Gale[25]	Non-destructive delayed neutron counting	8·1 ± 2·0	7·6 ± 1·3	24·6 ± 2	116·4 ± 4·7
Brunfelt and Steinnes[26]	I.N.A.A.	5·88	5·60	23·3	101
Morgan and Heier[27]	R.A.A.	6·47,	6·0,	24·1,	
	γ-Spectrometry	6·4	6·1	25·7	106
Gordon *et al.*[10]	I.N.A.A.	7·0 ± 0.5	6·7 ± 0·3	25·9 ± 0·5	125 ± 10
Greenland[24]	I.N.A.A.	6·6	5·8	26·0	120
Gangadharam and Parekh[5]	R.A.A.	6·43	5·85	21·2	—
Meyer[11]	I.N.A.A.				103·2 ± 3·3

R.A.A. = Radiochemical activation analysis
I.N.A.A. = Instrumental non-destructive activation analysis
γ-Spectrometry = Using natural γ-ray radioactivity.

TABLE II.—THORIUM CONTENT OF ZIRCON SAMPLES FROM INDIA

Code No.	Sample description	Thorium content *ppm*
Ch.Z.V.	Fine grained (−52 + 100 mesh) beach sand from Chavra, Kerala	114
MK.Z.V.	Fine grained (−52 + 100 mesh) beach sand from Manavalakurichi, Tamil Nadu	82
Kas.Z.B.	Brownish crystal of pegmatite origin from Kazipattanam, Andhra Pradesh	64
Pur.Z.D.	Detrital sand from Purulia, Bihar	85
Put.Z.A.	Brownish crystal of nepheline syenite origin from Puttuti, Kerala	63
Sev.Z.N.	Light brown crystal associated with anchoritic carbonatite from Sevathur, Tamil Nadu	245
Kan.Z.N.	Fine grained, brownish, of biotite migmatite origin from Kanyakumari, Tamil Nadu	117
Thad.Z.R.	Fine grained, dark violet, of biotite migmatite from Thadikarankonam, Tamil Nadu	239

standard. Replicate analyses of a zircon from Chavara gave an overall relative standard deviation of 6.4% for the method. A number of other zircons were also analysed by this method and the results are given in Table II.

The radiochemical purity of the ^{233}Pa isolated from the sample was established from the γ-ray spectrum, which revealed the absence of any peak not attributable to ^{233}Pa, the decay under the 310 keV photo-peak which gave a half-life of 27–28 days comparable with 27 days reported in the literature,[28] and the absence of gamma-active radio nuclides emitting photons of energy greater that 400 keV.

Acknowledgements—The authors wish to thank Mr. K. K. Dar, Director, Atomic Minerals Division, Government of India, Dr. U. A. Aswathanarayana, Professor of Geology, Sagar University and Dr. G. Boreswara Rao, Reader, Andhra University, for supplying the selected zircon specimens. We are particularly thankful to Mr. G. V. U. Rao and his colleagues of the Metallurgy Division, B.A.R.C. for their help in mineral separation and minerological analysis.

Analytical Division
Bhabha Atomic Research Centre
Modular Laboratories
Trombay, Bombay-85 (AS), *India*

H. B. DESAI
R. PARTHASARATHY
M. SANKAR DAS

Summary—The thorium content of zircons and standard rock samples was determined by neutron-activation analysis. The 310-keV photopeak activity of ^{233}Pa was enhanced by a prior chemical separation which removed interfering induced activities.

Zusammenfassung—Der Thoriumgehalt von Zirkonen und Standard-Gesteinsproben wurde durch Neutronenaktivierungsanalyse bestimmt. Die Aktivität des Photopeaks bei 310 keV von ^{233}Pa wurde durch eine vorausgehende chemische Abtrennung verstärkt, die gleichzeitig gebildete störende Aktivitäten entfernt.

Résumé—On a déterminé la teneur en thorium de zircons et d'échantillons de roche étalons par analyse par activation de neutrons. Le photopic d'activité 310 keV du ^{233}Pa a été exalté par une séparation chimique préalable qui élimine les activités induites gênantes.

REFERENCES

1. E. N. Jenkins, *Analyst*, 1955, **80**, 301.
2. V. H. Stark and C. Turkowsky, *Radiochim. Acta*, 1966, **5**, 16.
3. A. J. Travesí, J. Polomares and G. Dominguez, *Anal. Chim. Acta*, 1966, **35**, 421.
4. J. W. Morgan and J. F. Lovering, *ibid.*, 1963, **28**, 405.

5. E. V. Gangadharam and P. P. Parekh, *Radiochim. Acta*, 1968, **10**, 65.
6. T. W. Stern and H. J. Rose, Jr., *Am. Minerologist*, 1961, **46**, 606.
7. L. H. Ahrens, *Geochim. Cosmochim. Acta*, 1965, **29**, 711.
8. L. H. Ahrens, R. D. Cherry and A. J. Erlank, *ibid.*, 1967, **31**, 2379.
9. M. Mantel, P. Sung Tung and S. Amiel, *Anal. Chem.*, 1970, **42**, 267.
10. G. E. Gordon, K. Randle, G. G. Goles, J. B. Coriliss, M. H. Beeson and S. S. Oxley, *Geochim. Cosmochim. Acta*, 1968, **32**, 369.
11. H. G. Meyer, *J. Radioanal. Chem.*, 1971, **7**, 67.
12. K. A. Kraus, G. E. Moore and F. Nelson, *J. Am. Chem. Soc.*, 1956, **78**, 2692.
13. H. W. Kirby, *The Radiochemistry of Protactinium*, NAS-NS 3016, U.S.A.E.C. 1959.
14. S. J. Lyle and A. D. Shendrikar, *Talanta*, 1965, **12**, 573.
15. E. J. Cantanzaro, *Radiometric Dating for Geologists*, Eds. E. I. Mamilton and R. M. Farquhar, p. 225. Interscience, New York, 1968.
16. C. W. Sill, *Anal. Chem.*, 1966, **38**, 1458.
17. G. L. Bate, J. R. Huizenga and H. A. Portratz, *Geochim. Cosmochim. Acta*, 1959, **16**, 88.
18. M. Osawa, O. Tokunago, M. Tokunago, M. Itani and M. Sakanoue, *J. Nucl. Sci. Tech.*, 1966, **3**, 333.
19. D. N. Edgington, *Intern. J. Appl. Radiation Isotopes*, 1967, **18**, 11.
20. M. Picer and P. Strohal, *Anal. Chim. Acta*, 1968, **40**, 131.
21. L. Kosta and G. B. Cook, *Talanta*, 1965, **12**, 977.
22. F. Girardi and R. Pietra, *Anal. Chem.*, 1963, **35**, 173.
23. W. J. Ross, *ibid.*, 1964, **36**, 1114.
24. L. P. Greenland, from F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.
25. N. H. Gale, *Proc. Symp. Radioactive Dating and Methods of Low Level Counting*, IAEA, Vienna, 1967, p. 431.
26. A. O. Brunfelt and E. Steinnes, *Anal. Chim. Acta*, 1969, **48**, 13.
27. J. W. Morgan and K. S. Heier, *Earth Planet Sci. Letters* 1966, **1**, 158.
28. C. M. Lederer, J. M. Hollander and I. Perlman *Table of Isotopes*, Wiley, New York, 1967.

Talanta, 1972, Vol. 19, pp. 366 to 369. Pergamon Press. Printed in Northern Ireland

Spectrophotometric molybdenum determination with thiolactic acid*

(*Received* 15 *July* 1971. *Accepted* 22 *October* 1971)

THE DETERMINATION of molybdenum by estimating the yellow complex formed with thioglycollic acid was first described by Will and Yoe.[1] They found, however, that numerous ions interfere at concentrations less than 25 ppm. Přibil and Adam[2] eliminated many of these interferences by extracting the complex into a 5% Alamine 336-S solution and measuring the absorbance of the organic phase at 370 nm. Bismuth(III), mercury(II), tungsten(VI), chloride, fluoride and nitrate ions interfered.

Busev, Nacu and Redzit[3] used thiolactic acid (TLA) and some of its anilides for the colorimetric estimation of molybdenum. The molybdenum complex with TLA was extracted into an organic solvent in the presence of benzylthiuronium chloride. Molybdenum was successfully determined in the presence of any of nine different metal ions.

We have developed a simple spectrophotometric method for molybdenum that is more selective than the thioglycollic acid method[1] and is quicker and requires less manipulation than the extraction procedures.[2,3] The present method is also very selective.

EXPERIMENTAL

Reagents

α-Thiolactic acid (TLA) was obtained from Evans Chemetics, Inc. and used as received. The assay was reported as 99.4%.

Molybdenum(VI) solutions were prepared by dissolving MoO_3 in 7*M* ammonia solution and diluting to 500 ml. The 0.05*M* solutions of other metal ions were made by dissolving the appropriate salts in distilled water (slightly acidified). Tartaric acid (0.05*M*) was added to antimony(V), tin(IV), titanium(IV) and tungsten(VI) solutions to prevent hydrolysis.

---

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. *3057*.

5. E. V. Gangadharam and P. P. Parekh, *Radiochim. Acta*, 1968, **10**, 65.
6. T. W. Stern and H. J. Rose, Jr., *Am. Minerologist*, 1961, **46**, 606.
7. L. H. Ahrens, *Geochim. Cosmochim. Acta*, 1965, **29**, 711.
8. L. H. Ahrens, R. D. Cherry and A. J. Erlank, *ibid.*, 1967, **31**, 2379.
9. M. Mantel, P. Sung Tung and S. Amiel, *Anal. Chem.*, 1970, **42**, 267.
10. G. E. Gordon, K. Randle, G. G. Goles, J. B. Coriliss, M. H. Beeson and S. S. Oxley, *Geochim. Cosmochim. Acta*, 1968, **32**, 369.
11. H. G. Meyer, *J. Radioanal. Chem.*, 1971, **7**, 67.
12. K. A. Kraus, G. E. Moore and F. Nelson, *J. Am. Chem. Soc.*, 1956, **78**, 2692.
13. H. W. Kirby, *The Radiochemistry of Protactinium*, NAS-NS 3016, U.S.A.E.C. 1959.
14. S. J. Lyle and A. D. Shendrikar, *Talanta*, 1965, **12**, 573.
15. E. J. Cantanzaro, *Radiometric Dating for Geologists*, Eds. E. I. Mamilton and R. M. Farquhar, p. 225. Interscience, New York, 1968.
16. C. W. Sill, *Anal. Chem.*, 1966, **38**, 1458.
17. G. L. Bate, J. R. Huizenga and H. A. Portratz, *Geochim. Cosmochim. Acta*, 1959, **16**, 88.
18. M. Osawa, O. Tokunago, M. Tokunago, M. Itani and M. Sakanoue, *J. Nucl. Sci. Tech.*, 1966, **3**, 333.
19. D. N. Edgington, *Intern. J. Appl. Radiation Isotopes*, 1967, **18**, 11.
20. M. Picer and P. Strohal, *Anal. Chim. Acta*, 1968, **40**, 131.
21. L. Kosta and G. B. Cook, *Talanta*, 1965, **12**, 977.
22. F. Girardi and R. Pietra, *Anal. Chem.*, 1963, **35**, 173.
23. W. J. Ross, *ibid.*, 1964, **36**, 1114.
24. L. P. Greenland, from F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.
25. N. H. Gale, *Proc. Symp. Radioactive Dating and Methods of Low Level Counting*, IAEA, Vienna, 1967, p. 431.
26. A. O. Brunfelt and E. Steinnes, *Anal. Chim. Acta*, 1969, **48**, 13.
27. J. W. Morgan and K. S. Heier, *Earth Planet Sci. Letters* 1966, **1**, 158.
28. C. M. Lederer, J. M. Hollander and I. Perlman *Table of Isotopes*, Wiley, New York, 1967.

Talanta, 1972, Vol. 19, pp. 366 to 369. Pergamon Press. Printed in Northern Ireland

Spectrophotometric molybdenum determination with thiolactic acid*

(*Received* 15 *July* 1971. *Accepted* 22 *October* 1971)

THE DETERMINATION of molybdenum by estimating the yellow complex formed with thioglycollic acid was first described by Will and Yoe.[1] They found, however, that numerous ions interfere at concentrations less than 25 ppm. Přibil and Adam[2] eliminated many of these interferences by extracting the complex into a 5% Alamine 336-S solution and measuring the absorbance of the organic phase at 370 nm. Bismuth(III), mercury(II), tungsten(VI), chloride, fluoride and nitrate ions interfered.

Busev, Nacu and Redzit[3] used thiolactic acid (TLA) and some of its anilides for the colorimetric estimation of molybdenum. The molybdenum complex with TLA was extracted into an organic solvent in the presence of benzylthiuronium chloride. Molybdenum was successfully determined in the presence of any of nine different metal ions.

We have developed a simple spectrophotometric method for molybdenum that is more selective than the thioglycollic acid method[1] and is quicker and requires less manipulation than the extraction procedures.[2,3] The present method is also very selective.

EXPERIMENTAL

Reagents

α-Thiolactic acid (TLA) was obtained from Evans Chemetics, Inc. and used as received. The assay was reported as 99.4%.

Molybdenum(VI) solutions were prepared by dissolving MoO_3 in 7*M* ammonia solution and diluting to 500 ml. The 0.05*M* solutions of other metal ions were made by dissolving the appropriate salts in distilled water (slightly acidified). Tartaric acid (0.05*M*) was added to antimony(V), tin(IV), titanium(IV) and tungsten(VI) solutions to prevent hydrolysis.

---

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. *3057*.

Procedure

Take a sample containing 120–1920 μg of molybdenum and dilute to about 35 ml. Add a masking agent if copper, tungsten, iron or bismuth are present (Table I). Adjust the pH to between 1.0 and 1.6 with sulphuric acid, perchloric acid or sodium hydroxide. Transfer to a 50-ml volumetric flask, add 0.5 ml of TLA and dilute to volume with water. Measure the absorbance at 365 nm *vs* a blank.

TABLE I.—MASKING AGENTS USED IN REDUCING INTERFERENCE IN THE ABSORPTION OF THE TLA–Mo COMPLEX

Ion	Added, *mmole*	Masking agent	Added, *mmole*
Cu*	0.25	thiourea	2.4
Fe	0.25	H_3PO_4	1.5
Bi	0.25	EDTA	2.5
W	0.25	tartrate	1.0

* Absorbance must be measured within 10 min.

RESULTS AND DISCUSSION

Absorption spectra

Spectra of α-thiolactic acid and the TLA–molybdenum complex at pH 1.0 are shown in Fig. 1. The shoulder on the TLA–molybdenum spectrum is useful in the determination of molybdenum. A wavelength of 365 nm was found to be the most free from foreign ion interferences.

Effect of pH

Figure 2 shows the effect of pH on the absorbance of the TLA–Mo complex at a molybdenum concentration of $2 \times 10^{-4}M$. The chemistry of molybdenum is complex because of the polymerized species formed in acidic solutions. Therefore, no attempt was made to determine the cause for the deviation between pH 1.6 and 2.6. This phenomenon occurred in three separate experiments using perchloric, hydrochloric and sulphuric acid, respectively. A pH range of 1.0–1.6 was selected. The absorbance is less dependent on small changes in acidity within this range and there are fewer interferences than at higher pH values.

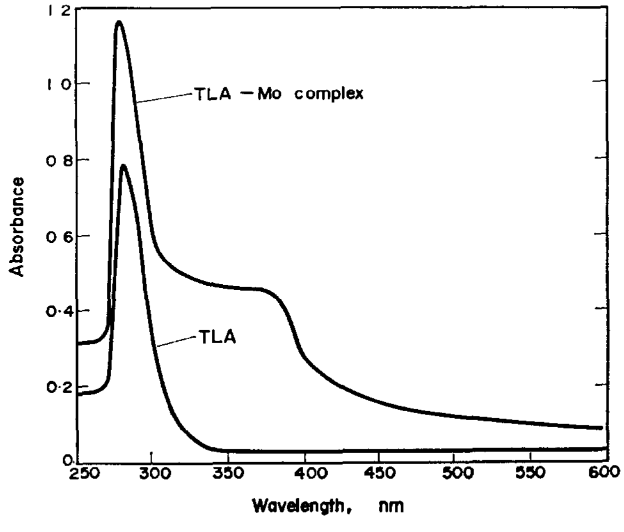


FIG. 1.—Absorption spectra of TLA and TLA–Mo complex in perchloric acid solution. (Mo = $2 \times 10^{-4}M$)

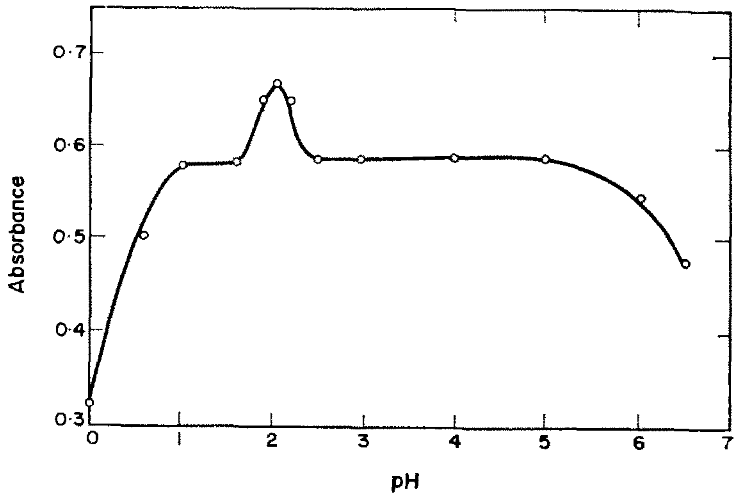


FIG. 2.—Effect of pH on the absorbance of the TLA-Mo complex. (Mo = 2 × $10^{-4}M$)

Stability

With thioglycollic acid as a colour-forming reagent for molybdenum, the solution became slightly turbid and this turbidity increased on standing. This did not occur when TLA was used. The TLA-molybdenum complex formed at pH 1.0–1.6 gave constant absorbance readings for more than 24 hr with no evidence of turbidity.

Beer's law

The complex obeyed Beer's law for molybdenum concentrations between 2.5×10^{-5} and $4 \times 10^{-4}M$. The molar absorptivity was 280 $\text{l.mole}^{-1}.\text{mm}^{-1}$ at 365 nm. At a pH of 1.0–1.6 this compares with a value of approximately 210 $\text{l.mole}^{-1}.\text{mm}^{-1}$ as calculated from the results of Will and Yoe at pH 1 for thioglycollic acid.

Effect of foreign ions

The absorbance of solutions containing 5 μmole of molybdenum and 500 times as much (2.5 mmole) of a foreign metal ion was measured. The following ions caused no interference: Na, Al, K, Ca, Cr(III), Ni, Zn, Ga, Sr, Y, Zr, Cd, La, Yb, Hf, Hg(II), Pb, Th. In sulphuric acid solution 2.5 mmole of tin(IV), antimony(V), or uranium(VI) caused no interference, but did interfere seriously in hydrochloric acid solution. Vanadium(V) and chromium(VI) were reduced to vanadium(IV) and chromium(III), respectively. These did not interfere with the determination of molybdenum if sufficient TLA was added to compensate for the amount consumed in the reduction.

Copper(II), tungsten(VI), iron(III) and bismuth caused some error in the molybdenum determination unless a suitable masking agent was added as listed in Table I. Phosphoric acid effectively masked iron(III), and thiourea masked copper(II) if the absorbance in the latter case was read within 10 min. Tungsten(VI) caused no error if tartrate was added, and bismuth did not interfere if EDTA was present. The effect of any combination of masking agents was not studied. Of the metal ions investigated, only gold(III), platinum(IV) and silver(I) interfered with the molybdenum determination.

The effect of several anions was investigated. Sulphate, perchlorate, phosphate or chloride (5.0 mmole), EDTA (2.5 mmole) and acetate, nitrate, tartrate, citrate (1.0 mmole) caused no error. Fluoride interfered by causing low results.

Acknowledgement—The aid of Evans Chemetics Inc. in supplying the thiolactic acid is gratefully acknowledged.

Iowa State University
Ames, Iowa, U.S.A.

JAMES S. FRITZ
DONALD R. BEUERMAN

Summary—A quick, selective method for molybdenum(VI) is based on the formation of a yellow thiolactic acid complex. The complex is formed at pH 1.0–1.6, and the absorbance is measured at 365 nm.

Zusammenfassung—Ein rasches selektives Bestimmungsverfahren für Molybdän(VI) beruht auf der Bildung eines gelben Komplexes mit Thiomilchsäure. Der Komplex bildet sich bei pH 1,0–1,6, seine Extinktion wird bei 365 nm gemessen.

Résumé—Une méthode rapide, sélective du molybdène(VI), est basée sur la formation d'un complexe jaune avec l'acide thiolactique. Le complexe se forme à pH 1,0–1,6 et l'on mesure l'absorption à 365 nm.

REFERENCES

1. F. Will and J. H. Yoe, *Anal. Chem.*, 1953, **25**, 1363.
2. R. Přibil and J. Adam, *Talanta*, 1971, **18**, 349.
3. A. I. Busev, A. Nacu and G. P. Rudzit, *Zh. Analit. Khim.*, 1964, **19**, 337.

Talanta, 1972, Vol. 19, pp. 369 to 372. Pergamon Press. Printed in Northern Ireland

Determination of traces of iron(II) in the presence of iron(III) by the bathophenanthroline method

(*Received* 4 *May* 1971. *Accepted* 17 *October* 1971)

THE BATHOPHENANTHROLINE method is generally used for determination of the sum of iron(II) and (III) in boiler water. In investigation of the deposition mechanism of iron oxides and corrosion of boiler tubes, it is necessary to know the concentration of the iron(II). Titration methods,[1] Clark's bathophenanthroline method[2] and the ammonium thiocyanate–thioglycol method[3] cannot be applied to boiler water, because the concentration of iron(II) is too low, of the order of ppM (parts per milliard). Lee's bathophenanthroline method[4] gave a positive error for solutions with a high ratio of iron(III) to iron(II).

The present paper describes attempts to determine iron(II) with bathophenanthroline after masking of iron(III).

EXPERIMENTAL

Reagents

A standard solution of iron(II) was prepared by dissolving reagent-grade ferrous ammonium sulphate in water acidified with sulphuric acid, and diluting with demineralized water. This solution was prepared daily, and was saturated with carbon dioxide and kept in an atmosphere of carbon dioxide. Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) was dissolved in isopropanol. Other chemicals were chemically pure or reagent-grade.

Procedure

Sample solution [200 ml, 0·2–6 μg of iron(II)] was adjusted to a pH between 4·2 and 4·7 with 2 ml of $3M$ hydrochloric acid and 5 ml of $2{\cdot}6M$ ammonium acetate, and transferred to a 300-ml separatory funnel; 2 ml of 2·5% w/v sodium pyrophosphate solution were added and the solution was left standing for 5 min for the iron(III) pyrophosphate complex to form. Then 2 ml of $0{\cdot}25M$ bathophenanthroline in isopropanol were added and the solution was shaken mechanically for 1 min; 25 ml of n-butanol were added and the shaking continued for 1 min. After settling (for 5 min) the aqueous phase was discarded, and 10 ml of methanol were added to the organic phase, which was then shaken to dissolve any water adherent to the funnel. The absorbance of the organic phase was measured in a 100-mm cell at 533 nm against a reagent blank.

RESULTS AND DISCUSSION

Choice of stabilizing agent

A major problem was to establish a solution environment that would keep the iron species in their original oxidation states. Several potential stabilizing agents including citrate, tartrate, oxalate, malonate, salicylate, phosphate and pyrophosphate were tested.

Summary—A quick, selective method for molybdenum(VI) is based on the formation of a yellow thiolactic acid complex. The complex is formed at pH 1.0–1.6, and the absorbance is measured at 365 nm.

Zusammenfassung—Ein rasches selektives Bestimmungsverfahren für Molybdän(VI) beruht auf der Bildung eines gelben Komplexes mit Thiomilchsäure. Der Komplex bildet sich bei pH 1,0–1,6, seine Extinktion wird bei 365 nm gemessen.

Résumé—Une méthode rapide, sélective du molybdène(VI), est basée sur la formation d'un complexe jaune avec l'acide thiolactique. Le complexe se forme à pH 1,0–1,6 et l'on mesure l'absorption à 365 nm.

REFERENCES

1. F. Will and J. H. Yoe, *Anal. Chem.*, 1953, **25**, 1363.
2. R. Přibil and J. Adam, *Talanta*, 1971, **18**, 349.
3. A. I. Busev, A. Nacu and G. P. Rudzit, *Zh. Analit. Khim.*, 1964, **19**, 337.

Talanta, 1972, Vol. 19, pp. 369 to 372. Pergamon Press. Printed in Northern Ireland

Determination of traces of iron(II) in the presence of iron(III) by the bathophenanthroline method

(*Received* 4 *May* 1971. *Accepted* 17 *October* 1971)

THE BATHOPHENANTHROLINE method is generally used for determination of the sum of iron(II) and (III) in boiler water. In investigation of the deposition mechanism of iron oxides and corrosion of boiler tubes, it is necessary to know the concentration of the iron(II). Titration methods,[1] Clark's bathophenanthroline method[2] and the ammonium thiocyanate–thioglycol method[3] cannot be applied to boiler water, because the concentration of iron(II) is too low, of the order of ppM (parts per milliard). Lee's bathophenanthroline method[4] gave a positive error for solutions with a high ratio of iron(III) to iron(II).

The present paper describes attempts to determine iron(II) with bathophenanthroline after masking of iron(III).

EXPERIMENTAL

Reagents

A standard solution of iron(II) was prepared by dissolving reagent-grade ferrous ammonium sulphate in water acidified with sulphuric acid, and diluting with demineralized water. This solution was prepared daily, and was saturated with carbon dioxide and kept in an atmosphere of carbon dioxide. Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) was dissolved in isopropanol. Other chemicals were chemically pure or reagent-grade.

Procedure

Sample solution [200 ml, 0·2–6 μg of iron(II)] was adjusted to a pH between 4·2 and 4·7 with 2 ml of $3M$ hydrochloric acid and 5 ml of $2{\cdot}6M$ ammonium acetate, and transferred to a 300-ml separatory funnel; 2 ml of 2·5% w/v sodium pyrophosphate solution were added and the solution was left standing for 5 min for the iron(III) pyrophosphate complex to form. Then 2 ml of $0{\cdot}25M$ bathophenanthroline in isopropanol were added and the solution was shaken mechanically for 1 min; 25 ml of n-butanol were added and the shaking continued for 1 min. After settling (for 5 min) the aqueous phase was discarded, and 10 ml of methanol were added to the organic phase, which was then shaken to dissolve any water adherent to the funnel. The absorbance of the organic phase was measured in a 100-mm cell at 533 nm against a reagent blank.

RESULTS AND DISCUSSION

Choice of stabilizing agent

A major problem was to establish a solution environment that would keep the iron species in their original oxidation states. Several potential stabilizing agents including citrate, tartrate, oxalate, malonate, salicylate, phosphate and pyrophosphate were tested.

Only pyrophosphate masked iron(III) without suppressing the colour reaction or reducing iron(III).

Choice of solvent

The ferrous bathophenanthroline complex has usually been extracted with isopentanol and any droplets of water in the extract have been dissolved with isopropanol. However, when pyrophosphate is used, the colour of the isopentanol–isopropanol extract is unstable. Chloroform, carbon tetrachloride, n-hexanol, n-butanol, ketones and esters were tested as extraction solvents, and isopropanol, ethanol and methanol as solvents for residual water.

With solvents other than alcohols no coloured product was extracted. Even with alcohols as solvents, the colour faded with time, and a relationship existed between the rate of fading and the molar concentration of hydroxyl groups (sum of alcohol and water OH groups) in the organic phase. Although no explanation for this relationship was forthcoming, it appeared that the lower alcohols gave the more stable colour. Therefore n-butanol and methanol were the solvents selected.

The shaking time required for the complete formation of ferrous bathophenanthroline complex was about 2 min and after shaking, its colour showed no change for 15 min and then increased.

Effect of sodium pyrophosphate

Figure 1 shows the effect of sodium pyrophosphate on the absorbance for solutions containing iron(II) with and without iron(III). In the range from 2·6 to 60 mg sodium pyrophosphate masked iron(III) and permitted iron(II) to react with bathophenanthroline. Therefore, 25 mg (1 ml of 2·5% solution) were used in further work. This amount was adequate to prevent interference of iron(III) in up to 20-fold ratio to iron(II) if a 10% error could be tolerated (Table I). However, the masking reaction is not instantaneous, taking ~3 min at 15° and ~2 min at 20°. At 32° the absorbance begins to fall at ~6 min reaction time, so 5 min were allowed at room temperature. The time needed for

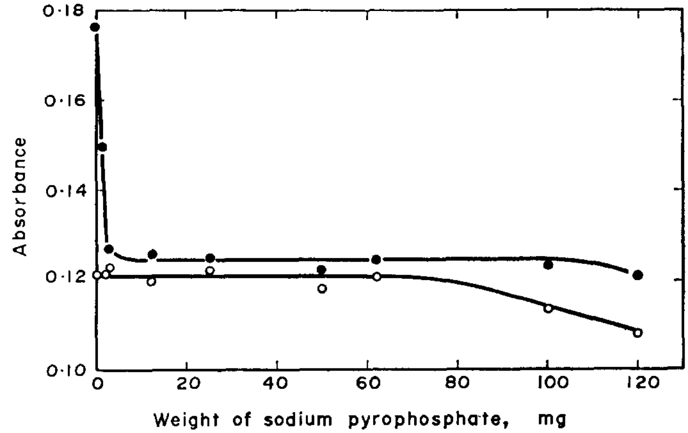


FIG. 1.—Effect of sodium pyrophosphate.
●—Fe(II) 5 ppM, Fe(III) 25 ppM: ○—Fe(II) 5 ppM.

TABLE I.—EFFECT OF IRON(III) ON ABSORBANCE OF IRON(II) COMPLEX

[Fe(III)]/[Fe(II)] in aqueous phase	Absorbance of Fe(II) complex			
	1 *ppM*	5 *ppM*	5* *ppM*	30 *ppM*
0	0·026	0·121	0·129	0·703
1	0·028	0·124	0·134	—
5	0·029	0·125	0·176	0·710
10	0·028	0·125	0·233	—
20	0·028	0·130	—	0·734
40	0·030	0·129	—	0·741
60	0·037	0·138	—	0·780

* Sodium pyrophosphate was not added.

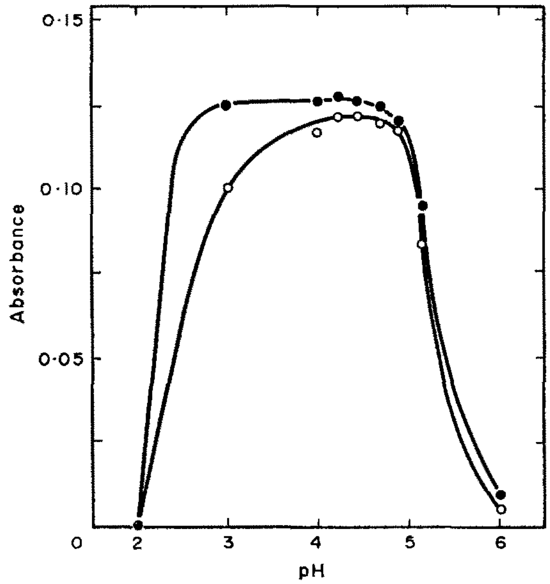


FIG. 2.—Effect of pH.
●—Fe(II) 5 ppM, Fe(III) 50 ppM: ○—Fe(II) 5 ppM.

complete extraction was 2 min; the absorbance remained constant for 15 min but then gradually increased.

Effect of pH

The absorbance was unaffected by pH in the range 3·0–4·7 if iron(III) was originally present and 4·2–4·7 if it was absent (Fig. 2). The latter range was therefore used.

Absorption spectrum and stability of the colour

The absorption maximum was at 533 nm and the molar absorptivity was $2 \cdot 03 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$, slightly less than in isopentanol-isopropanol medium. Beer's law was obeyed for iron(II) concentrations up to 30 ppM in the aqueous solution (coefficient of variation 4% for 5 ppM). The absorbance in n-butanol is constant for 20 min and for at least 3 hr in butanol-methanol.

Effect of diverse ions

As shown in Table I, nickel, zinc, manganese(II) and chromium(III) had little effect on the absorbance. Copper(II) gave a negative error, because it catalysed the oxidation of ferrous ion with oxygen. Cobalt(II) gave a positive error, because cobalt reduced ferric ion in the presence of bathophenanthroline.[3] Only 25 ppM of copper and 5 ppM of cobalt could be tolerated.

Technical Laboratory TAKAYUKI MIZUNO
Central Research Institute of Electrical Power Industry
Iwato, Komae Tokyo, Japan

Summary—Traces of iron(II) (1–30 ppM) in the presence of iron(III) were determined (error <10%) by the bathophenanthroline method. Interference of iron(III) was eliminated by masking with sodium pyrophosphate (2·5–60 mg). The iron(II) complex was extracted with n-butanol, at pH 4·2–4·7.

Zusammenfassung—Spuren des Eisen(II) (1–30 ppM) in Gegenwart des Eisen(III) wurden mit Bathophenanthrolin Methode bestimmt (Fehler <10%). Störung von Eisen(III) wurde mittels Maskierung mit Natriumpyrophosphate (2,5–60 mg) beseitigt. Eisen(II) Komplex wurde in n-butanol, at pH 4,2–4,7 extrahiert.

Résumé—On a déterminé trace de fer(II) (1–30 ppM) en présence de fer(III) (erreur 10%) par la méthode de bathopénanthroline. On a éliminé l'interférence de fer(III) par la dissimulation avec pyrophosphate de sodium (2,5–60 mg). On a extrait la complexe de fer(II) avec n-butanol à pH 4,2–4,7.

REFERENCES

1. Vereinigung der Grosskesselbesitzer. *Analysenverfahren für den Kraftwerksbetrieb*, p. 240. Vulkan Verlag Dr. W. Classen, Essen, 1962.
2. L. J. Clark, *Anal. Chem.*, 1962, **34**, 348.
3. *JIS* K0101-1966, p. 96.
4. G. F. Lee and W. Stumm, *J. Am. Water Works Ass.*, 1960, **52**, 1567.

Talanta, 1972, Vol. 19, pp. 372 to 377. Pergamon Press. Printed in Northern Ireland

Determination of inorganic impurities in vinyl chloride by activation analysis

(*Received* 15 *March* 1971. *Accepted* 24 *June* 1971)

THE LACK of experimental data concerning the traces of inorganic compounds found in vinyl chloride is due to the difficulties in using classical analytical methods on gases or liquids at low temperature for the detection of trace impurities. The object of this paper is to examine the estimation of trace inorganic impurities in vinyl chloride. The high sensitivity of the activation method compared with the usual chemical methods makes it suitable for this purpose. The vinyl chloride obtained by synthesis from acetylene and hydrogen chloride (mercuric chloride as catalyst) is likely to be contaminated by such inorganic constituents as arsenic and phosphorus which are present in acetylene as AsH_3 and PH_3.

A vinyl chloride sample irradiated with a thermal neutron flux gives mainly one radioactive isotope, ^{38}Cl, *via* an (n, γ) reaction, in high yield.[1] For an irradiation time of a few hours all other nuclear reactions may be neglected. The presence of elements other than C, H and Cl (*e.g.*, As) might lead to the formation of radioisotopes which could be determined.

A slow neutron flux of $1{\cdot}2 \times 10^9$ n/mm²/sec with a fast neutron component of $6{\cdot}2 \times 10^7$ n/mm²/sec was used. Under these conditions the existence of nuclear reactions such as (n, α) and (n, p) for chlorine are possible and could result in the formation of ^{32}P and ^{35}S, the first of which would interfere in the determination of phosphorus by β-counting. The (n, p) reaction occurs even with slow neutrons but a cross-section for reactor neutrons of 590 ± 90 mb is given.[2] The effect of ^{35}S is easily eliminated, owing to its low β-energy of 0·2 MeV. ^{32}P may result either from the $^{31}P(n, \gamma)^{32}P$ reaction (which is directly related to the phosphorus present as impurity) or from $^{35}Cl(n, \alpha)^{32}P$. The contribution of the latter nuclear reaction is low, owing to the subcadmium neutron spectrum having a cross-section of 0·08 mb.[3] In the presence of fast neutrons this value might be higher.

EXPERIMENTAL

Sample irradiation

Vinyl chloride samples were introduced into quartz vials cooled with liquid nitrogen in a special aluminium vessel insulated with expanded polystyrene. In order to keep the sample cool the facility of adding further refrigerant was required and the only reactor channel suitable for this purpose had the low neutron flux of 10^7 n/mm²/sec and could not be used for analytical determinations. This difficulty was overcome by taking advantage of the tendency of the liquid monomer to polymerize. This polymer is solid and stable at 25° and could be used as the sample in the normal channel which has a neutron flux of $1{\cdot}2 \times 10^9$ n/mm²/sec.

The industrial synthesis of vinyl chloride uses acetylene and hydrogen chloride. Acetylene is contaminated by AsH_3 and PH_3 generated from calcium arsenide and phosphide present in calcium carbide. The acetylene and hydrogen chloride are also contaminated with traces of oxygen, which can give oxygenated compounds. Other organic contaminants of the monomer may be produced during the reaction process. These organic compounds and, more efficiently, vinyl chloride react with arsine and phosphine, resulting in the retention of these elements in the polymer. The same is true for bromine (existing as HBr in HCl).

Résumé—On a déterminé trace de fer(II) (1–30 ppM) en présence de fer(III) (erreur 10%) par la méthode de bathopénanthroline. On a éliminé l'interférence de fer(III) par la dissimulation avec pyrophosphate de sodium (2,5–60 mg). On a extrait la complexe de fer(II) avec n-butanol à pH 4,2–4,7.

REFERENCES

1. Vereinigung der Grosskesselbesitzer. *Analysenverfahren für den Kraftwerksbetrieb*, p. 240. Vulkan Verlag Dr. W. Classen, Essen, 1962.
2. L. J. Clark, *Anal. Chem.*, 1962, **34**, 348.
3. *JIS* K0101-1966, p. 96.
4. G. F. Lee and W. Stumm, *J. Am. Water Works Ass.*, 1960, **52**, 1567.

Talanta, 1972, Vol. 19, pp. 372 to 377. Pergamon Press. Printed in Northern Ireland

Determination of inorganic impurities in vinyl chloride by activation analysis

(*Received* 15 *March* 1971. *Accepted* 24 *June* 1971)

THE LACK of experimental data concerning the traces of inorganic compounds found in vinyl chloride is due to the difficulties in using classical analytical methods on gases or liquids at low temperature for the detection of trace impurities. The object of this paper is to examine the estimation of trace inorganic impurities in vinyl chloride. The high sensitivity of the activation method compared with the usual chemical methods makes it suitable for this purpose. The vinyl chloride obtained by synthesis from acetylene and hydrogen chloride (mercuric chloride as catalyst) is likely to be contaminated by such inorganic constituents as arsenic and phosphorus which are present in acetylene as AsH_3 and PH_3.

A vinyl chloride sample irradiated with a thermal neutron flux gives mainly one radioactive isotope, ^{38}Cl, *via* an (n, γ) reaction, in high yield.[1] For an irradiation time of a few hours all other nuclear reactions may be neglected. The presence of elements other than C, H and Cl (*e.g.*, As) might lead to the formation of radioisotopes which could be determined.

A slow neutron flux of $1{\cdot}2 \times 10^9$ n/mm²/sec with a fast neutron component of $6{\cdot}2 \times 10^7$ n/mm²/sec was used. Under these conditions the existence of nuclear reactions such as (n, α) and (n, p) for chlorine are possible and could result in the formation of ^{32}P and ^{35}S, the first of which would interfere in the determination of phosphorus by β-counting. The (n, p) reaction occurs even with slow neutrons but a cross-section for reactor neutrons of 590 ± 90 mb is given.[2] The effect of ^{35}S is easily eliminated, owing to its low β-energy of 0·2 MeV. ^{32}P may result either from the $^{31}P(n, \gamma)^{32}P$ reaction (which is directly related to the phosphorus present as impurity) or from $^{35}Cl(n, \alpha)^{32}P$. The contribution of the latter nuclear reaction is low, owing to the subcadmium neutron spectrum having a cross-section of 0·08 mb.[3] In the presence of fast neutrons this value might be higher.

EXPERIMENTAL

Sample irradiation

Vinyl chloride samples were introduced into quartz vials cooled with liquid nitrogen in a special aluminium vessel insulated with expanded polystyrene. In order to keep the sample cool the facility of adding further refrigerant was required and the only reactor channel suitable for this purpose had the low neutron flux of 10^7 n/mm²/sec and could not be used for analytical determinations. This difficulty was overcome by taking advantage of the tendency of the liquid monomer to polymerize. This polymer is solid and stable at 25° and could be used as the sample in the normal channel which has a neutron flux of $1{\cdot}2 \times 10^9$ n/mm²/sec.

The industrial synthesis of vinyl chloride uses acetylene and hydrogen chloride. Acetylene is contaminated by AsH_3 and PH_3 generated from calcium arsenide and phosphide present in calcium carbide. The acetylene and hydrogen chloride are also contaminated with traces of oxygen, which can give oxygenated compounds. Other organic contaminants of the monomer may be produced during the reaction process. These organic compounds and, more efficiently, vinyl chloride react with arsine and phosphine, resulting in the retention of these elements in the polymer. The same is true for bromine (existing as HBr in HCl).

Standards

Preliminary qualitative determinations identified the inorganic contaminants as arsenic, bromine and phosphorus.

Standards of As_2O_3, KBr, HCl and Na_2HPO_4 were irradiated at the same time as the samples, under similar conditions to avoid errors due to neutron flux fluctuations, shielding effects, geometry and time interval.

Radioactivity measurements

Most of the radioactivity measurements were based on gamma spectrometry with a 42 × 45 mm NaI(Tl) scintillation counter associated with a 400-channel pulse-height analyser (SA-40 B, Intertechnique). A 25 $\mu g/mm^2$ end-window GM counter for β-measurements was also used for ^{32}P. Liquefied samples were counted in a special apparatus cooled with liquid nitrogen.

RESULTS AND DISCUSSION

When liquefied monomer has been irradiated (usually for 3 hr) the resulting γ-ray spectrum is similar to that shown in Fig. 1. The presence of ^{38}Cl(37·3-min half-life) from the nuclear reaction $^{37}Cl(n, \gamma)$ ^{38}Cl is evident and does not permit an estimation of any inorganic component. When ^{38}Cl has completely decayed, the existence of the peaks is revealed at energies of 0·56, 0·78, 1·04, 1·2, 1·7, and 2·17 MeV (spectrum 2).

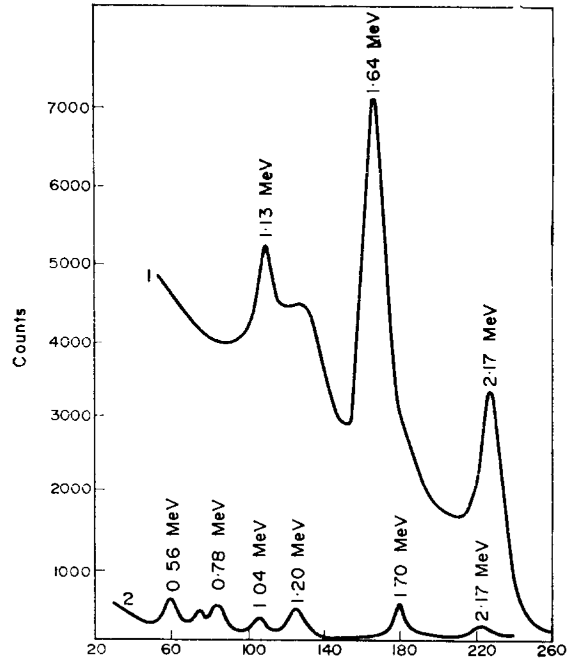


FIG. 1.—Liquefied monomer gamma-spectra.
1. In the presence of ^{38}Cl.
2. In the absence of ^{38}Cl.

From nuclear data,[1,4] the peaks at 0·56, 0·66 and perhaps 1·2 MeV are ascribed to ^{76}As. The remaining peaks cannot be ascribed to ^{76}As because of the low activities involved. The height of the 0·56-MeV peak is inexplicable,[4] but the low neutron flux resulted in bad counting statistics. The alternative method of irradiation of polyvinyl chloride was therefore used. The counting statistics were thus improved owing to an increased neutron flux and a larger sample size. The γ-spectra obtained for sample and standard are illustrated in Fig. 2.

By comparison with literature data it is clear that ^{76}As obtained in the nuclear reaction[1,4] $^{75}As(n, \gamma)$ ^{76}As is not the only component involved. The ^{82}Br must also be taken into consideration with its

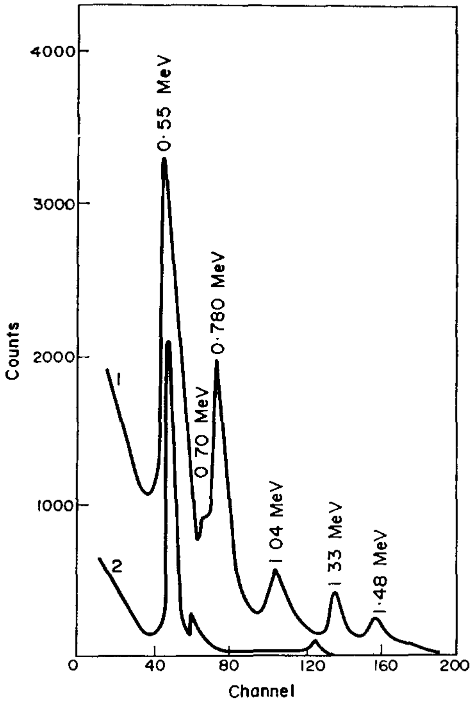


Fig. 2.—Gamma-spectra.
1. Solid polymerized sample.
2. ^{76}As gamma spectrum induced in standard.

characteristic peaks at 0·55, 0·70, 0·78, 1·04, 1·33 and 1·48 MeV (higher energies are neglected),[4] as shown in Fig. 2. This proves the existence of the nuclear reaction ^{81}Br(n, γ) ^{82}Br. The target element abundance 49·46% ^{81}Br and $\sigma = 3{\cdot}3$ b explain the presence of this component.[1] A decay curve for the 0·78 and 1·04-MeV peaks, which except for the 0·55-MeV peak are the most important, gave a half-life of 35·4 hr, characteristic of ^{82}Br.

The 0·55-MeV peak results from the superposition of the ^{76}As 0·56-MeV peak and the ^{82}Br 0·55-MeV peak. A decay curve for the ^{76}As peak gave a half-life of 31 hr. Because of the half-lives of ^{76}As of 26·4 hr,[1] and ^{82}Br of 35·4 hr,[1] it is clear that both components are present and this fact is reflected in the half-life of 31 hr found. If this peak alone is used the two activities must be determined separately, which is not possible from the decay curve obtained. A mathematical treatment permits the estimation of the activities of two components at time $t = 0$ when their half-lives are known.[5] The total activity I (measured) is a resultant of the two components I_1 and I_2 given in equation (1)

$$I = I_1 \exp(-\lambda_1 t) + I_2 \exp(-\lambda_2 t) \tag{1}$$

where the λ's are the disintegration constants.

Dividing this equation by $\exp(-\lambda_1 t)$ gives

$$I \exp(\lambda_1 t) = I_1 + I_2 \exp[(\lambda_1 - \lambda_2)t] \tag{2}$$

A plot of $I \exp(\lambda_1 t)$ against $\exp[(\lambda_1 - \lambda_2)t]$ gives the total activity at $t = 0$, when $I = I_1^0 + I_2^0$, as an intercept on the ordinate. The slope gives I_2^0.

The values obtained for one example were ^{76}As, $I_1^0 = 1{\cdot}7 \times 10^4$ c/Δt; ^{82}Br, $I_2^0 = 3{\cdot}60 \times 10^4$ c/Δt. The results for 3 experiments are given in Table I. In this case the value of I_1^0 for ^{76}As from equation (2) was compared with the corresponding 0·56-MeV peak activity of the standard.

For the bromine determination two methods have been used. In the first, potassium bromide was used as the standard and the peak at 0·78 MeV was the most suitable to use because it involved the highest activity (except for the 0·55-MeV peak). The corresponding peaks of sample and standard were compared and the results are given in Table I. The second method was employed to check the

TABLE I.—DETERMINATION OF ARSENIC AND BROMINE
(Sample weight 354 mg and 302 mg compared with 2·5 mg As_2O_3 and 3·0 mg KBr as standards)

No. of sample	Activity in sample ^{76}As *counts/20 min*	Activity in sample ^{82}Br *counts/20 min*	Activity in standard ^{76}As *counts/20 min*	Activity in standard ^{82}Br *counts/20 min*	Impurity in sample As %	Impurity in sample Br %
1	$1{\cdot}7 \times 10^4$	$1{\cdot}5 \times 10^4$	$1{\cdot}23 \times 10^7$	$2{\cdot}98 \times 10^6$	$7{\cdot}4 \times 10^{-4}$	$2{\cdot}86 \times 10^{-3}$
2	$1{\cdot}55 \times 10^4$	$1{\cdot}35 \times 10^4$	$1{\cdot}13 \times 10^7$	$2{\cdot}75 \times 10^6$	$8{\cdot}6 \times 10^{-4}$	$3{\cdot}27 \times 10^{-3}$
3	$1{\cdot}45 \times 10^4$	$1{\cdot}28 \times 10^4$	$1{\cdot}10 \times 10^7$	$2{\cdot}67 \times 10^6$	$8{\cdot}2 \times 10^{-4}$	$3{\cdot}20 \times 10^{-3}$

Mean value for As $(8{\cdot}0 \pm 0{\cdot}6) \times 10^{-4}$ %
Mean value for Br $(3{\cdot}07 \pm 0{\cdot}2) \times 10^{-3}$ %

TABLE II.—DETERMINATION OF BROMINE
(Based on activities at $t = 0$ from equation (2), using As_2O_3 as standard)

No. of sample	Activities at $t = 0$ ^{76}As *counts*	Activities at $t = 0$ ^{82}Br *counts*	Impurity in sample As %	Impurity in sample Br %
1	17000	36000	$7{\cdot}4 \times 10^{-4}$	$6{\cdot}25 \times 10^{-3}$
2	14500	20000	$8{\cdot}2 \times 10^{-4}$	$4{\cdot}55 \times 10^{-3}$
3	15500	21500	$8{\cdot}6 \times 10^{-4}$	$4{\cdot}75 \times 10^{-3}$

Mean value for Br $(5{\cdot}4 \pm 0{\cdot}85) \times 10^{-3}$ %

results obtained for bromine, starting with the ^{76}As determination. The activity dN/dt induced in the target is given by the formula:

$$dN/dt = N\sigma\phi[1 - \exp(-\lambda t_1)] \qquad (3)$$

where N refers to the target quantity (abundance included) σ is the cross-section, ϕ the flux and t_1 the time of irradiation. The activity A measured with a scintillation counter for the time interval Δt at time t_2 is given by:

$$A = N\sigma\phi[1 - \exp(-\lambda t_1)] \exp(-\lambda t_2)\Omega\eta\Delta t \qquad (4)$$

where Ω includes the geometry and the scattering effects and η is the photopeak efficiency.

It would be convenient to write two equations of type (4); one for arsenic and one for bromine. Their ratio would eliminate several constants which are the same in both cases. The only unknown would be the quantity of bromine, which is deduced from the amount of arsenic previously determined (Table I) and the activities of ^{76}As and ^{82}Br found from equation (2). The results are given in Table II.

It must be emphasized that this alternative method is a check on the values obtained but the differences between the bromine results obtained by the two methods result from variations in cross-sections, geometry and statistics. The cross-section is referred to thermal neutrons, not to reactor neutrons, and a substantial error might thereby result. The fluctuations from the mean value in Tables I and II are acceptable under the given experimental conditions.

A note of caution must be introduced in estimating ^{76}As. In the presence of fast neutrons ($6{\cdot}2 \times 10^7$ n/mm^2/sec) and bromine as contaminant, the following nuclear reaction is theoretically possible: $^{79}Br(n, \alpha)\,^{76}As$. However, owing to the low amount of bromine present (the same order of magnitude as the arsenic), the lower fast-neutron flux and the much lower cross-section, the presence of this nuclear reaction is certainly not detectable. The neutron spectrum of energies, combined with the reaction threshold, leads to the virtual absence of (n, α) reactions.

When all other radioactive products have decayed, the only components supposed to be present are ^{35}S and ^{32}P. The former was obtained in the $^{35}Cl(n, p)^{35}S$ reaction even with slow neutrons. The second radioisotope is more likely to result with fast neutrons in the $^{35}Cl(n, \alpha)\,^{32}P$ nuclear process. Interference of the last reaction with the $^{31}P(n, \gamma)\,^{32}P$ reaction which permits the estimation of the phosphorus impurity may be expected and steps taken to avoid this contribution.

The vinyl chloride sample was irradiated at the same time as hydrogen chloride and Na_2HPO_4 as standards. The pure hydrochloric acid leads to ^{35}S and ^{32}P following (n, p) and (n, α) nuclear reactions. The same is true for the sample, including the $^{31}P(n, \gamma)\,^{32}P$ reaction which occurs in the presence of phosphorus as impurity. The Na_2HPO_4 standard is used for the (n, γ) reaction of phosphorus. In all

TABLE III.—DETERMINATION OF PHOSPHORUS
(Sample weight 302 mg, using Na_2HPO_4 and HCl solution as standards. P = 4·3 mg and Cl = 172 mg)

No. of sample	Sample activity	HCl activity	Sample activity due to P	Activity of 4·3–mg P standard	P impurity in sample
	counts/172 *mg* Cl		*counts*/172 *mg* Cl	*counts*	%
1	3250	2970	280	21600	$1{\cdot}85 \times 10^{-2}$
2	3050	2760	290	19300	$2{\cdot}14 \times 10^{-2}$

Mean value $(2{\cdot}0 \pm 0{\cdot}15) \times 10^{-2}$ %

cases a reasonable decay time was allowed before counting, in order to eliminate the effect of interfering radioactive products.

Beta-counting was later employed and a decay and absorption curve followed. When the decay curve was measured, an absorber (aluminium) was used to eliminate the effect of ^{35}S. The half-life determined in the classical way gave a value of 14·3 d ± 5%.

When hydrochloric acid activity was subtracted from that of the sample, the ^{32}P and ^{35}S contributions were eliminated. The residual activity was ascribed to the (n, γ) reaction of the phosphorus impurity, which is compared with the standard activity. For the purposes of calculation, it was preferred to eliminate some undesirable weak activities by absorption with aluminium. Results of the phosphorus determination are given in Table III.

CONCLUSIONS

The thermal-neutron activation method used has permitted the estimation of arsenic and bromine by gamma-spectrometry and phosphorus by beta counting. In each case the fluctuations from the mean value are 10–20%. Discrepancies between the values obtained by the two methods of calculation are explained by side-effects and the influence of the cross-sections.

Institute of Atomic Physics
Bucharest, Romania

FLORIN T. BUNUŞ
SANDA MURGALESCU

Summary—Trace impurities in vinyl chloride have been determined by activation analysis in a reactor thermal neutron flux of $1{\cdot}2 \times 10^9$ n/mm²/sec. Irradiations were carried out on liquid and solid samples at the same time as a standard. Gamma-spectrometry was used to reveal the presence of arsenic and bromine, the quantitative estimation being based on two calculus methods., The impurities determined were: arsenic $8{\cdot}0 \pm 0{\cdot}6 \times 10^{-4}$%, bromine $3{\cdot}07 \pm 0{\cdot}2 \times 10^{-3}$% and phosphorus $2{\cdot}0 \pm 0{\cdot}15 \times 10^{-2}$%.

Zusammenfassung—Spuren-Verunreinigungen in Vinylchlorid wurden aktivierungsanalytisch bei einem thermischen Neutronenfluß von $1{,}2 \times 10^9$ n/mm²/sec im Reaktor bestimmt. Die Bestrahlungen wurden an flüssigen und festen Proben gleichzeitig mit einem Standard ausgeführt. Mit Hilfe der Gamma-Spektrometrie wurde Arsen und Brom nachgewiesen, wobei für die quantitative Auswertung zwei Verfahren zur Anwendung kamen. Folgende Verunreinigungen wurden bestimmt: Arsen $8{,}0 \pm 0{,}6 \times 10^{-4}$%, Brom $3{,}07 \pm 0{,}2 \times 10^{-3}$% und Phosphor $2{,}0 \pm 0{,}15 \times 10^{-2}$%.

Résumé—On a déterminé des impuretés à l'état de traces dans le chlorure de vinyle par analyse par activation dans un flux de neutrons thermiques de réacteur de $1{,}2 \times 10^9$ n/mm²/s. Les irradiations ont ete effectuées sur des échantillons liquides et solides en même temps que sur un étalon. On a utilisé la spectrométrie gamma pour révéler la présence d'arsenic et de brome, l'estimation quantitative étant basée sur deux méthodes de calcul. On a déterminé les impuretés suivantes: arsenic $8{,}0 \pm 0{,}6 \times 10^{-4}$%, brome $3{,}07 \pm 0{,}2 \times 10^{-3}$% et phosphore $2{,}0 \pm 0{,}15 \times 10^{-2}$%.

REFERENCES

1. *Der Bundesminister fur Wissenschaftliche Forschung, Nuklidkarte,* 3rd Ed. Bonn, 1968.
2. R. W. Durham and F. Girardi, *Nuovo Cimento Suppl.*, 1961 **19,** 4.
3. *Neutron Cross Sections* BNL-325, Suppl. 2, Vol.1, 2nd. Ed.
4. C. E. Crouthamel, *Applied Gamma Ray Spectrometry,* Pergamon, Oxford, 1960.
5. G. R. Martin, *Private communication.*
6. F. T. Bunuş, *M. Sc. Thesis,* University of Durham, 1962.

Talanta, 1972, Vol. 19, pp. 377 to 379. Pergamon Press. Printed in Northern Ireland

Organic and inorganic ion-exchange beads as indicators in redox and precipitation titrations

(*Received* 30 *April* 1971. *Accepted* 21 *October* 1971)

RECENTLY ion-exchange resins have found some new analytical applications in the detection of metal ions.[1] Resin beads, loaded with indicators, have also been used for the titration of acids and bases,[2,3] but, so far as we are aware, have not been used as indicators in precipitation titrations.

Some inorganic ion-exchangers show great selectivity towards some metal ions, and adsorb them irreversibly. In these cases the metal ion is probably incorporated in the matrix and the bead of the exchanger in this particular form can be used advantageously as an indicator. Thus stannic arsenate adsorbs iron(III) irreversibly,[4] and in this form can be used for titration of metal ions with ferrocyanide.

EXPERIMENTAL

Reagents

Potassium ferrocyanide. The trihydrate was dried at 100° for 1 hr. A $0{\cdot}10M$ ferrocyanide solution was prepared by exact weighing and 1 g of sodium carbonate was added per litre.

Zinc sulphate, $0{\cdot}1M$. Standardized with EDTA.

Ferrous ammonium sulphate, $0{\cdot}1M$.

Potassium dichromate, $0{\cdot}1N$.

Silver nitrate, $0{\cdot}1M$.

Ceric sulphate solution. Standardized against arsenious oxide. Nitrates of other metal ions were used.

Resin beads. Dowex 50W × 8 (20–50 mesh) resin beads in Na^+ form were soaked in alcoholic diphenylamine solution, and in H^+ form were soaked in *p*-dimethylaminobenzylidenerhodanine, for use in redox and argentometric titrations respectively.

Procedures

Determination of Zn, Pb, Ag *and* Cd. To the metal ion solutions were added 5 ml of appropriate acid solution ($1M$ acetic for lead, silver and cadmium and $1M$ hydrochloric for zinc), 1 ml of distilled alcohol and 3 or 4 beads in the Fe(III) form. The solutions were titrated with potassium ferrocyanide from a 5-ml microburette. Near the end-point the solution was vigorously shaken after the addition of each drop. A sharp change from yellow to blue on the beads occurred at the end-point owing to the formation of Prussian Blue. For titrant concentrations of $0{\cdot}005$–$0{\cdot}1M$ and metal ion amounts of 0·01–1 m mole the titration error was from 0 to +0·4%.

Titration of Fe(II) *or* $Na_2S_2O_3$. To 5 ml of Fe(II) solution were added 5 ml of $5N$ sulphuric acid, 1 ml of 85% phosphoric acid and 3 or 4 beads in the diphenylamine form. The solution was titrated with potassium dichromate, ceric sulphate, or potassium permanganate from a 5-ml microburette with vigorous shaking after each drop. The end-point colour change from yellow to blue on the resin surface is sharp. The titrant concentration was varied between 0·005 and $0{\cdot}1N$, but the error remained more or less constant in the range +0·2–0·5%,

Determination of Cl^-, Br^-, I^-. To 5 ml of metal halide solution were added a few *p*-dimethylaminobenzylidenerhodanine beads. In the case of chloride and bromide 5 ml of alcohol were also added. On titration with silver nitrate there was a sharp colour change from yellow to violet orange at the end-point. The results are in error by +0·1–0·3%

Successive determination of Zn^{2+} *and* Cl^-. To a mixture of zinc chloride and sodium chloride 5 ml of alcohol and a few *p*-dimethylaminobenzylidenerohdanine beads were added. The solution

REFERENCES

1. *Der Bundesminister fur Wissenschaftliche Forschung*, *Nuklidkarte*, 3rd Ed. Bonn, 1968.
2. R. W. Durham and F. Girardi, *Nuovo Cimento Suppl.*, 1961 **19**, 4.
3. *Neutron Cross Sections* BNL-325, Suppl. 2, Vol.1, 2nd. Ed.
4. C. E. Crouthamel, *Applied Gamma Ray Spectrometry*, Pergamon, Oxford, 1960.
5. G. R. Martin, *Private communication.*
6. F. T. Bunuş, *M. Sc. Thesis*, University of Durham, 1962.

Talanta, 1972, Vol. 19, pp. 377 to 379. Pergamon Press. Printed in Northern Ireland

Organic and inorganic ion-exchange beads as indicators in redox and precipitation titrations

(*Received* 30 *April* 1971. *Accepted* 21 *October* 1971)

RECENTLY ion-exchange resins have found some new analytical applications in the detection of metal ions.[1] Resin beads, loaded with indicators, have also been used for the titration of acids and bases,[2,3] but, so far as we are aware, have not been used as indicators in precipitation titrations.

Some inorganic ion-exchangers show great selectivity towards some metal ions, and adsorb them irreversibly. In these cases the metal ion is probably incorporated in the matrix and the bead of the exchanger in this particular form can be used advantageously as an indicator. Thus stannic arsenate adsorbs iron(III) irreversibly,[4] and in this form can be used for titration of metal ions with ferrocyanide.

EXPERIMENTAL

Reagents

Potassium ferrocyanide. The trihydrate was dried at 100° for 1 hr. A 0·10*M* ferrocyanide solution was prepared by exact weighing and 1 g of sodium carbonate was added per litre.

Zinc sulphate, 0·1*M*. Standardized with EDTA.

Ferrous ammonium sulphate, 0·1*M*.

Potassium dichromate, 0·1*N*.

Silver nitrate, 0·1*M*.

Ceric sulphate solution. Standardized against arsenious oxide. Nitrates of other metal ions were used.

Resin beads. Dowex 50W × 8 (20–50 mesh) resin beads in Na^+ form were soaked in alcoholic diphenylamine solution, and in H^+ form were soaked in *p*-dimethylaminobenzylidenerhodanine, for use in redox and argentometric titrations respectively.

Procedures

Determination of Zn, Pb, Ag *and* Cd. To the metal ion solutions were added 5 ml of appropriate acid solution (1*M* acetic for lead, silver and cadmium and 1*M* hydrochloric for zinc), 1 ml of distilled alcohol and 3 or 4 beads in the Fe(III) form. The solutions were titrated with potassium ferrocyanide from a 5-ml microburette. Near the end-point the solution was vigorously shaken after the addition of each drop. A sharp change from yellow to blue on the beads occurred at the end-point owing to the formation of Prussian Blue. For titrant concentrations of 0·005–0·1*M* and metal ion amounts of 0·01–1 m mole the titration error was from 0 to +0·4%.

Titration of Fe(II) *or* $Na_2S_2O_3$. To 5 ml of Fe(II) solution were added 5 ml of 5*N* sulphuric acid, 1 ml of 85% phosphoric acid and 3 or 4 beads in the diphenylamine form. The solution was titrated with potassium dichromate, ceric sulphate, or potassium permanganate from a 5-ml microburette with vigorous shaking after each drop. The end-point colour change from yellow to blue on the resin surface is sharp. The titrant concentration was varied between 0·005 and 0·1*N*, but the error remained more or less constant in the range +0·2–0·5%,

Determination of Cl^-, Br^-, I^-. To 5 ml of metal halide solution were added a few *p*-dimethylaminobenzylidenerhodanine beads. In the case of chloride and bromide 5 ml of alcohol were also added. On titration with silver nitrate there was a sharp colour change from yellow to violet orange at the end-point. The results are in error by +0·1–0·3%

Successive determination of Zn^{2+} *and* Cl^-. To a mixture of zinc chloride and sodium chloride 5 ml of alcohol and a few *p*-dimethylaminobenzylidenerohdanine beads were added. The solution was titrated with silver nitrate till a sharp colour change from yellow to violet on the resin phase was observed. Then 5 ml of 1M hydrochloric acid were added. The slight excess of silver ions present at the equivalence point, was precipitated as the chloride, and a few Fe(III)-form beads were added and zinc was titrated with ferrocyanide. The results are reasonable, the errors for Cl^- being in the range from −3·0 to +0·2% and for zinc(II) from −1·2 to +0·5%.

Simultaneous determination of silver and lead. A silver nitrate–lead nitrate mixture was taken in a burette and added drop by drop to a known volume of sodium chloride solution containing 5 ml of ethanol and resin beads in the *p*-dimethylaminobenzylidenerhodanine form. At the equivalence point silver was precipitated as the chloride and lead nitrate remained in solution. A few drops of sodium chloride were added at the equivalence point to precipitate excess of silver (to minimize the error in the determination of lead), 5 ml of 1M acetic acid were added and lead was titrated with potassium ferrocyanide, with Fe(III) beads as indicator. The errors are from 0 to +0·3% for silver and from −0·7 to 0·90 for lead. Chloride solutions (0·001N) can be titrated with 0·005–0·001N silver with an error of +0·3–0·9%.

Determination of chloride in a coloured solution. The chloride in a cobalt(II)–chloride mixture is determined as above. The addition of a few ml of saturated cobalt nitrate solution intensifies the colour but does not effect the end-point.

Effect of diverse ions in Zn *determination.* To 5 ml of 0·002M zinc solution the following ions were added in the quantities (in mg) given in parentheses. No interference in the zinc determination was noticed when *p*-dimethylaminobenzylidenerhodanine was used as an indicator: Ba^{2+}(100), Sr^{2+}(100), Na^+(240), Al^{3+}(40), Ca^{2+}(120), NH_4^+(40). Thiosulphate, chlorate, perchlorate, sulphite, thiosulphate and thiocyanate do not interfere.

The following ions did not interfere at the levels indicated when stannic arsenate beads were used: Ba^{2+}(120), Al^{3+}(60), NH_4^+(60), Na^+(320) Ca^{2+}(140).

Care must be taken that a drop of titrant does not fall on the resin beads. A blank correction was made in each case. The results are summarized in Table I.

TABLE I.—COMPARISON OF THE BEAD METHOD WITH VOLHARD'S METHOD IN THE TITRATION OF Cl^- IN $CoCl_2$

Volhard method			Proposed method		
Chloride taken, *mg*	Chloride found, *mg*	Error %	Chloride taken, *mg*	Chloride found, *mg*	Error, %
6·35	3·19	−49	6·35	6·30	−0·7
12·78	9·58	−25	12·78	12·80	+0·1
9·58	6·55	−30	9·58	9·60	+0·2

DISCUSSION

In the determination of halides the method is superior to the Mohr method since chloride, bromide and iodide can be accurately titrated, and Mohr's method is not applicable to the determination of iodides and thiocyanates. Further the Mohr titration is possible only in the pH range of 7–10·5, whereas the bead method can be used with accuracy from pH 2 to 7. At pH less than 2 the method is inaccurate. Volhard's method is undoubtedly superior to Mohr's method, but it cannot be used if the solution itself has an intense colour. Thus in the titration of cobalt chloride the Volhard method gives wrong results whereas the bead method is accurate. It is also superior to the adsorption indicator method, since it is possible to titrate 0·001M chloride solution by this method. It is not possible to titrate chloride solution more dilute than 0·005M, using fluoroscein as indicator.

Another novel feature is that resin beads can be used for the successive determination of two substances. Thus zinc and chloride or silver and lead can also be determined without prior separation. This is feasible because it is possible to add different indicators in succession. This is not the case with the conventional indicators.

Another advantage is that selective, specific and sensitive spot test reagents can be appropriately used for volumetric titrations. The use of *p*-dimethylaminobenzylidenerhodanine is a case in point. It has been used for the titration of silver nitrate with potassium chloride or bromide in 6M nitric acid or 5M sulphuric acid.[5]

The greatest advantage of resin bead indicators is that a single indicator can be used when different species are titrated with the same titrant. Thus Zn, Pb, Ag, Cd and Cu have been titrated, using resin beads in the Fe(III) form as the indicator.

The method is particularly useful in dilute solutions, where the precipitates are not so dense and the colour change on the beads can be easily detected at the equivalence point. In more concentrated solutions, the beads are not visible through the thick precipitate, but the colour change on the resin phase can be seen by raising the beaker above eye level and viewing the beads at the bottom.

As zinc ferrocyanide is more soluble than Prussian Blue, the end-point is obtained rather early when zinc is titrated with ferrocyanide in aqueous medium and the results are erroneous. However if alcohol is added before the titration is started, accurate results are obtained, because the alcohol lowers the solubility product of zinc ferrocyanide. It will also lower the solubility product of iron(III) ferrocyanide but presumably to a lesser extent. Addition of alcohol may similarly improve the end-point for Pb, Ag and Cd titration. The addition of alcohol has a remarkable effect on the interference by diverse ions. Thus without alcohol barium interfered in the zinc titration even in 1:1 ratio, but in the presence of alcohol even 100 times as much did not interfere. The same is true for other ions. This is because the addition of alcohol suppresses the ionization of these electrolytes and prevents their interference. Stannic arsenate beads give even better results. Since Fe(III) is irreversibly adsorbed, the addition of large quantities of interfering ions does not affect the titrations.

Acknowledgements—The authors are grateful to Dr. S. M. F. Rahman for research facilities and to Mr. Virendra Kumar for many helpful suggestions.

Chemistry Department
Aligarh Muslim University
Aligarh, (U.P.) India

MOHSIN QURESHI
SAIDUL ZAFAR QURESHI
NIGHAT ZEHRA

Summary—Resin beads in the Fe(III) or *p*-dimethylaminobenzylidenerhodanine form are used as indicators in precipitation titrations with $K_3Fe(CN)_6$ and Ag^+. Resin beads with diphenylamine adsorbed on them can be used as indicators in cerimetric titrations. They have some advantages over conventional indicators.

Zusammenfassung—Harzperlen in der Fe(III)- oder in der p-Dimethylaminobenzylidenrhodamin-Form werden als Indikatoren bei Fällungstitrationen mit $K_3Fe(CN)_6$ und Ag^+ verwendet. Harzperlen mit adsorbiertem Diphenylamin können als Indikatoren bei cerimetrischen Titrationen verwendet werden. Sie haben gegenüber herkömmlichen Indikatoren einige Vorteile.

Résumé—On utilise des perles de résine sous la forme Fe(III) ou *p*-diméthylaminobenzylidène rhodamine comme indicateurs dans les titrages par précipitation avec $K_3Fe(CN)_6$ et Ag^+. On peut utiliser les perles de résine ayant adsorbé de la diphénylamine comme indicateurs dans les titrages cérimétriques. Elles ont quelques avantages par rapport aux indicateurs usuels.

REFERENCES

1. M. Fujimoto, *Chemist-Analyst*, 1960, **49**, 58.
2. P. W. Miller, *Anal. Chem.*, 1958, **30**, 1462.
3. L. Légrádi, *Magy. Kem. Folyoirat*, 1960, **66**, 76.
4. M. Qureshi, R. Kumar and H. S. Rathore, *J. Chem. Soc.* (*A*), 1970, 272.
5. H. Goto and S. Sato, *J. Chem. Soc. Japan*, 1946, **67**, 5.

Talanta, 1972, Vol. 19, pp. 381 to 382. Pergamon Press. Printed in Northern Ireland

ANNOTATION

On the analytical utility of quasi-linear molecular emission spectra

(*Received* 15 *July* 1971. *Accepted* 21 *October* 1971)

A UNIQUE development regarding the spectra of aromatic hydrocarbons was reported by a Russian spectroscopist, E. V. Shpol'skii about two decades ago.[1] Certain aromatic molecules, when frozen in a crystalline matrix of selected n-paraffin solvents, gave unusually well-resolved fine-structured luminescence emission spectra. This phenomenon, known as the Shpol'skii effect, was soon confirmed by others.[2] Two review articles appeared a few years later and generated considerable interest.[3,4]

The appearance of very sharp lines (5–10 cm^{-1} half-bandwidth) in the luminescence emission spectra of molecules in rigid n-paraffin solvents at low temperatures has been attributed to the embedding of a solute molecule in the crystalline lattice of the solvent, thereby rendering it much like an oriented gas molecule. When the molecular dimensions of the solute and solvent are very similar, the probability of observing quasi-linear spectra is greatly enhanced.[4,5]

In the last three years, more than 40 scientific papers have appeared on the subject of the Shpol'skii effect. Several[6,7] have strongly suggested widespread analytical application; few, however, have presented a detailed description of a specific analytical method along with the usual data stating reproducibility, accuracy and precision. Perhaps the closest approach to a true utilization of the Shpol'skii effect for an analytical determination is that of Muel and Lacroix;[8] 3,4-benzopyrene in cigarette smoke was determined, with octane used as solvent at −190°. A standard addition procedure was employed, using the sharp emission line of 3,4-benzopyrene at 403·0 nm. The reported limit of detection was 0·1 ng/ml with a relative precision of 10%. Some question, however, remains whether (under the experimental conditions used for the analysis) the fine structure, *i.e.*, "quasi-line spectra" observed, differed significantly from that obtained in an ordinary low-temperature fluorescence spectrum, because 3,4-benzopyrene exhibits fine structure in many solvents at low temperature.

We wish to offer some possible explanations for the absence of widespread utilization of the Shpol'skii effect in analytical chemistry. On the basis of much experimental evidence and a survey of the recent literature, we have reached the following conclusions regarding the analytical utility of the Shpol'skii effect.

(*i*) The availability of suitable commercial luminescence instrumentation severely limits analytical applications. Because quasi-line spectra generally exhibit half-band widths smaller than 0·1 nm, an instrument of very high resolution is necessary. To be analytically useful, the instrument must also have a high light-gathering power. Such an instrument can be prohibitively expensive. When spectra are obtained with instruments having lesser resolving power, little difference in the width of lines of the emission spectra is observed for the same molecule in many different solvents. In addition, molecules exhibiting the Shpol'skii effect generally give luminescence emission spectra possessing a reasonable amount of structure in many different solvents anyway, and so the gain in recorded spectral structure of molecules in solvents exhibiting the Shpol'skii effect is minimal with most analytical luminescence spectrometric systems.

(*ii*) At the present time, the efforts necessary for preparation of the unknown sample,[8] choice of solvent[4,5] and consideration of little studied matrix effects[9] on the intensity of low-temperature quasi-linear luminescence spectra must be unduly great.

(*iii*) Intensity of luminescence of quasi-line spectra often has an irregular and non-reproducible concentration dependence. Shpol'skii *et al.*[10] and Bolotonikova[11] have discussed the effects of molecular aggregation and energy transfer on the intensity of quasi-line spectra. They reported a reasonable luminescence intensity due to the Shpol'skii effect in the 10^{-3}–$10^{-2}M$ concentration region. At lower concentrations, band spectra from molecules aggregated inhomogeneously in the sample and not incorporated into the crystalline matrix may obscure the line spectra. Also, at concentrations above about $10^{-2}M$, the molecular aggregates absorb strongly but do not emit, whereas quasi-line spectra can only be observed from molecules incorporated in the solvent crystal lattice.

(*iv*) In addition to the solvent–solute restrictions regarding molecular size, and formation of molecular aggregates, problems arise with respect to the rate of freezing of solutions. Dokunikhin *et al.*[12] reported on the dependence of both intensity and width of quasi-lines as a function of the rate of freezing.

In light of the findings by the Russian workers[10-12] regarding the dependence of the intensity and width of quasi-lines, and of the results of a concerted effort on our part, we feel that under the experimental conditions normally employed in luminescence analysis there exists little difference between low-temperature emission spectra and the spectra expected as a result of the Shpol'skii effect. We feel at the same time that there are advantages of low-temperature luminescence in analysis but that one must be careful to distinguish between true quasi-line spectra and fine-structured emission resulting from a simple temperature effect.

It is our belief that combined instrumental and theoretical restrictions limit the usefulness of true quasi-line spectra for analytical determinations. Use of the Shpol'skii effect for qualitative identification purposes may prove to be of much greater use, although considerable caution must still be used in the interpretation of spectra.

Acknowledgement—Research was carried out as part of a study on the phosphorimetric analysis of drugs in blood and urine, supported by a U.S. Public Health Service Grant, GM 11373-08.

Department of Chemistry
University of Florida
Gainesville, Florida 32601, *U.S.A.*

R. J. LUKASIEWICZ
J. D. WINEFORDNER®

Summary—The analytical utility of the Shpol'skii effect has been examined. It is concluded that the combined instrumental and theoretical restrictions limit the analytical usefulness of true quasi-line spectra for quantitative work.

Zusammenfassung—Der analytische Nutzen des Shpol'skii-Effekts wurde untersucht. Es wird der Schluß gezogen, daß sowohl instrumentelle als auch theoretische Einschränkungen den analytischen Nutzen wahrer Quasi-Linienspektren beim quantitativen Arbeiten begrenzen.

Résumé—On a examiné l'utilité analytique de l'effet Shpol'skii. On en conclut que les restrictions instrumentales et théoriques combinées limitent l'intérêt analytique des spectres de quasi-raies vrais pour le travail quantitatif.

REFERENCES

1. E. V. Shpol'skii, A. A. Ll'ind and L. A. Klimova, *Dokl. Akad. Nauk SSR*, 1952, **87**, 935.
2. E. J. Bowen and B. J. Brocklehurst, *J. Chem. Soc.*, 1954, 3875.
3. E. V. Shpol'skii, *Soviet Phys. Usp.* (*Eng. Trans.*) 1959, **2**, 378.
4. *Idem*, *ibid.*, 1963, **6**, 255.
5. C. A. Parker, *Photoluminescence of Solutions*, Elsevier, New York, 1968.
6. J. Jaeger, *Atoms Environ.*, 1968, **2**, 293.
7. R. A. Passwater, *Fluorescence News*, 1971, **5**, (5), 4.
8. B. Muel and G. Lacroix, *Bull. Soc. Chim. France*, 1960, 2139.
9. R. Zweidinger and J. D. Winefordner, *Anal. Chem.*, 1970, **42**, 639.
10. E. V. Shpol'skii, L. A. Klimova, G. N. Nersesova and V. I. Glyodkoskii, *Opt. Spectry. USSR*, 1968, **24**, 25.
11. T. N. Bolonikova and T. M. Naumova, *ibid.*, 1968, **24**, 253.
12. N. S. Dokunikhin, V. A. Kizel, M. N. Sapozhnekov and S. L. Soloda, *ibid.*, 1967, **23**, 42.

Talanta, 1972, Vol. 19, p. 383. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

A rapid volumetric method for determination of thallium(I)

SIR,

During investigation of the complexation tendency of thallium(I) and (III) with certain sulphur compounds such as thiourea, thioglycollic acid, dithio-oxamide and thiosemicarbazide, it became necessary to develop a rapid and accurate method for the determination of thallium(I). In the bromine method[1] use is made of phenol or sulphosalicylic acid to destroy the excess of bromine remaining after oxidation of thallium(I) to thallium(III). This involves formation of undesirable precipitates. We have found that dimethylsulphoxide (DMSO) destroys almost immediately the excess of bromine, in the cold. DMSO and its oxidation product dimethylsulphone remain in solution and cause no interference in the iodometric titration of thallium(III). Based on this, a rapid and accurate method for the determination of thallium(I) in many oxide and co-ordination systems has been developed and satisfactorily used in these laboratories for over two years. The results obtained are correct to within 0·5%.

The recommended method is as follows. A sample containing 0·5–1 mmole of thallium(I) is dissolved or suspended in about 50 ml of 0·5*M* hydrochloric acid. Excess of bromine water (15–30 ml of 0·1*N*) is added, the mixture is swirled for a minute, then 2–3 ml of dimethylsulphoxide are added to destroy the unutilized bromine. After a minute, 15 ml of 10% potassium iodide solution are added and the iodine liberated by the thallium(III) is titrated with standard thiosulphate, after addition of 10 ml of 2% starch solution.

Department of Chemistry
Indian Institute of Technology
Madras-36, *India*
23 *September* 1971

M. CHANDRASEKHARAN
V. R. S. RAO
G. ARAVAMUDAN

REFERENCE

1. R. P. Buck, S. Farrington and E. Swift, *Anal. Chem.*, 1952, **24**, 1195.

Talanta, 1972, Vol. 19, pp. 385 to 390. Pergamon Press. Printed in Northern Ireland

ANALYTICAL CHEMISTRY IN JAPAN

TAITIRO FUJINAGA
Department of Chemistry, Faculty of Science, University of Kyoto, Kyoto, Japan

IN JAPAN, "Chemistry" did not exist until 1837, when Yoan Utagawa, an official scholar of the Tokugawa Government, published the first chemistry book, *Shamitsu Kaiso*. He writes in its introduction as follows.

"What is chemistry? It is a field of science in Western countries. Japan and China have not had such learning. It is chemistry that makes the characteristics of materials clear by decomposing and synthesizing them. It can be said that chemists are able not only to clarify the scheme designed by Nature, but also to participate in the work of Nature. The domain of chemistry is quite extensive and is neighbour to physics; when the physicist is unable to clarify the characteristics of a material by observing it from without, the chemist analyses it and makes clear Nature's scheme."

Shamitsu Kaiso is believed to be the translation of *Elements of Experimental Chemistry*, written by W. Henry, which had been translated into Dutch. At that time Dutch was the only foreign language permitted by the Tokugawa Government and this book was imported and translated into Japanese. Therefore, chemistry in Japan can be said to have arisen in England. The book contains five main chapters and one additional chapter. In the additional chapter qualitative analysis, preparative chemistry and mineral water analysis are described. The names of persons and substances were coined by Utagawa in Chinese characters. For example nitrogen was written as azoticum 亞曹知究母. This way of thinking has become the basis for the contemporary chemical terms of Japan. Owing to this fact, we are able to learn not only chemistry but also all fields of science in our mother tongue, a condition which has not always been realized in most of the nations of Asia.

For example, *Handbook of Analytical Chemistry*, edited by Prof. Kenjiro Kimura and published last year by the Japan Society for Analytical Chemistry, presents a tremendous amount of analytical data together with precise descriptions of most of the analytical methodologies, in 1,610 pages. *Encyclopedia of Analytical Chemistry*, edited by Prof. Soichiro Musha and published also last year by Kyoritsu Shuppan Co. Ltd., contains 12,000 terms with 2,544 figures in 2,228 pages, the equivalent of which may not be found even in the Western languages.

Education

In 1868, right after the Meiji Restoration, the government founded the Imperial Institute of Chemistry and later successively nine Imperial Universities, beginning with Tokyo in 1877, followed by various local main cities. There the course of chemistry was initiated and studied from the beginning at the Faculty of Science. In analytical chemistry, a professorial chair was first introduced in 1918 at the Department of Chemistry, Faculty of Science in the Imperial University of Tohoku, next in 1922 in Kyoto, in 1925 in Tokyo, in 1932 in Hokkaido, in 1941 in Kyushu, in 1942 in Nagoya and finally in Osaka. Likewise at most of the universities the course of analytical chemistry was introduced and studied similarly to the other fields of chemistry.

Meanwhile, in many universities courses of analytical chemistry were initiated in the faculties of engineering, pharmacology, medicine, agriculture and liberal arts. For instance, at the Faculty of Engineering of the University of Tokyo they have three chairs of analytical chemistry in their Department of Industrial Chemistry. Besides faculties, some ancillary institutes in the universities have chairs of analytical chemistry. Thus in one university there are more than ten professors working in the field of analytical chemistry, with an equivalent number of associate professors and twice as many instructors and assistants.

Before World War II there were nine Imperial Universities, including those in Souel and Taipei. General MacArthur, at the time of the occupation of Japan, thought that seven Imperial Universities were too few and status-prone: he felt the necessity of establishing universities in every prefecture of Japan, which can be compared to the state university system in the United States. In spite of Japan being a small country, the number of prefectures is almost the same as the number of states in the U.S.A. and seventy-five governmental universities and thirty-two other public universities were established (after the War the adjective "Imperial" was replaced by "governmental"). He also thought that private universities should have equal authority with the governmental universities, and so two hundred and eighty-one private universities have been founded. Most of these universities have more than one chair of analytical chemistry. This university policy as well as the establishment of the Japanese Constitution can be said to be one of the most successful decisions which have greatly contributed to today's peace and prosperity in Japan. Needless to say, this decision also contributed basically to the development of analytical chemistry: the Japanese Government and her Ministry of Education going along with the policy, advised the establishment of a division of analytical chemistry in the Department of Chemistry for all universities, irrespective of whether they were public or private. Even at present many leading chemists in Japan believe that analytical chemistry is the basis of chemistry, and that the "systematic qualitative analysis" originated by Noyes should be the first step of practice for students to become capable researchers. However, in spite of the fact that the educational level and the research facilities for analytical chemistry have made a remarkable progress both in quality and quantity, recent students seem to have lost interest in learning and researching on the methodology of analytical chemistry.

Research

Thanks to the increase of universities and hence the number of analytical professors, analytical chemistry has been greatly developed, followed by great progress in instrumentation in this field. However, it is hardly possible to describe the whole picture of the development of analytical chemistry in Japan, so the lineage in the Faculties of Science in the former Imperial Universities will be briefly introduced. At the University of Tohoku, Professor Emeritus Matsusuke Kobayshi, who is the foundation-holder of the chair, initiated the use of liquid amalgam for the reduction of metals in place of the solid amalgam of the Jones reductor: this modification has been applied to many practical analyses after thorough experimental and theoretical treatment. Professor Em. Shinichiro Hakomori, who introduced electrometric methods and cathode ray luminescence analysis, succeeded to this position, followed by Professor

Em. Yoshinaga Oka, who introduced γ-ray activation analysis besides many investigations in the field of chemical analysis. The position is now held by Professor Nobuo Suzuki, who is studying mainly the solvent effect in the extraction process, and substoichiometric determinations. At the University of Kyoto the late Professor Em. Motooki Matsui developed electrochemistry as applied to oragnic synthesis and inorganic analysis. Professor Em. Masayoshi Ishibashi succeeded to this position and contributed to the development of instrumental analysis, especially in the field of inorganic polarography. He also applied co-precipitation phenomena and instrumental analysis to the study of oceanography, determining more than 50 elements in sea-water, among which 17 elements were discovered there for the first time. After Prof. Ishibashi's retirement Professor Taitiro Fujinaga succeeded to his chair, and is mainly studying new electrochemical methodologies such as current-scan polarography, electrolytic chromatography, non-aqueous solvent voltammetry, *etc.* At the University of Tokyo Professor Em. Kenjiro Kimura was the first holder of the chair of analytical chemistry and performed extensive instrumental research, especially in the fields of X-ray and emission spectroscopy, and radiochemical analysis with his colleague Professor Em. Eiichi Minami, who succeeded to his position. They have also contributed to the development of geochemistry, especially that of hot springs in Japan. After their retirement, Professor Shizuo Fujiwara succeeded to the position and is studying mainly the nuclear magnetic and electron spin resonance spectroscopy as applied to analytical chemistry. At the University of Hokkaido, Professor Em. Yasumitsu Uzumasa initiated the analytical chemistry division and studied mainly emission and absorption spectroscopy, applied to geochemical analysis of hot springs and volcanic substances. The position then passed to Professor Tomihiko Kambara who is mainly studying the diffusion processes related to polarography and gas chromatography. At the University of Kyushu, Professor Sakae Shinoda, who mainly studied X-ray analysis of rare earth elements, Professor Iwaji Iwasaki who developed trace analysis applied to geochemical samples, and Professor Jun Yoshimura who mainly investigated the use of ion-exchange resins applied to inorganic analysis, have occupied the chair of analytical chemistry. Professor Shigeru Ohashi is now working mainly on gel-permeation chromatography as applied to the analysis of inorganic complexes. At the University of Nagoya, Professor Em. Ken Sugawara founded the division and concentrated on the development of trace analysis applied to the analysis of lake, river and spring water. The position is now held by Professor Motoharu Tanaka who is mainly interested in equilibrium studies on various titration and extraction processes. At the University of Osaka, Professor Shigero Ikeda is working on various problems in electron spectroscopy (ESCA) and electroanalytical chemistry in non-aqueous solvents. It should be emphasized that many achievements in the development of analytical chemistry have also been realized in other faculties and universities. Here let me quote one example. At the Faculty of Agriculture of the University of Kyoto, the late Professor Masuzo Shikata devised the polarograph with Professor Jaroslav Heyrovský in Prague in 1924, and next year the first commercial model was made by the Yanagimoto Mfg. Co. under his guidance. Professor Shikata with his successor Professor Em. Isamu Tachi initiated the study of organic polarography and contributed much to the development of polarography in this country: they established the Polarographic Society of Japan in 1960 and publish bimonthly the *Review of Polarography* in English.

Industrial analysis

In 1900 the Tokyo Industrial Research Institute (IRI) was established and later several IRI's were founded in Osaka and other main cities, which have taken charge of the analyses requested by the public. In the Tokyo IRI, the Analytical Chemistry Centre was established in 1957. There are many kinds of new analytical instruments and up-to-date machinery on display and used for furthering research. President Dr. Yoichiro Mashiko is making a big effort for its further development.

In 1925 the first Japanese Engineering Standard (JES), on the *Analysis of Copper-base Alloys*, appeared, and was followed by many series of other JES. After World War II these standards have been succeeded by the Japanese Industrial Standards (JIS). The JIS give criteria for various practical methods of analysis to be applied to raw materials and industrial products. Professor Em. Takayuki Somiya of the University of Tokyo, Faculty of Engineering, contributed much to the development of applied analytical chemistry and process control in industry. This position was then held by Professor Hitoshi Kamata, who is working mainly on emission spectroscopy and mass spectroscopy applied to industrial analysis. Professor Em. Hidehiro Goto of the University of Tohoku made a big contribution to the study of trace analysis, using spectrophotometric and catalytic methods, which were applied to the analysis of iron and steel. Overall, the analytical laboratories of industrial factories, research institutes and universities have been rapidly improved in these decades. For example most of the iron and steel works are equipped with an automatic emission spectrometric analyser, the so-called "Quantometer" together with a pneumatic sample conveyer and telephone reply system between smelting furnace and laboratory. With this facility, the production quality is finely controlled while the melt is still hot. This kind of rapid analysis is widely adopted in various industries and even further automated by use of computers. The contribution of analytical chemistry to the study of environmental science is also worth mentioning: such analytical information on flowing water as degree of transparency (photometric), chemical oxygen demands (coulometric), pH (glass electrode), dissolved oxygen (amperometric), cyanide (ion-selective electrode) and electrical conductivity, *etc*, are automatically recorded at unmanned stations on rivers and lakes. The records are sent to the central analytical laboratory, through cable if necessary. Air pollution due to carbon monoxide, sulphur dioxide (infrared absorption) and oxidants (coulometric) is also analysed automatically and in many cities shown to the public with a digital electric sign.

Analytical instrument industries

Most of the large analytical instruments and pure chemicals for analytical purposes had to be imported before World War II. On the other hand the first model of a polarograph, designed by Professor Shikata, was commercialized in 1925 almost at the same time that Nejedley in Czechoslovakia sold the world's first commercial model. Likewise the background of the present prosperity in the industry of analytical instruments had been slowly growing up. The expansion of analytical instruments in the market is remarkable in these decades: Yanagimoto Mfg. Co. is now selling a series of polarographs which can be linked in a single frame unit to give the complete range of direct current, alternative current, square-wave and radiofrequency-modulated square-wave polarograms. Shimazu Mfg. Co. manufactures X-ray fluorescence spectrometers, including an electron microprobe analyser and various kinds of automated emission and absorption spectrometers. Hitachi Mfg. Co. produces a mass spectrometer, electron microscope and other chromatographic and optical instruments. Japan Electronics and Optical Laboratories Inc. is well known for its nuclear magnetic and electron spin resonance spectrometers. In the field of reagent chemicals, Wakojunyaku Co., Tokyo Kasei Kogyo Co. and Dojindo Co. have developed many kinds of organic reagents, especially chelating agents, which are supplied to overseas customers. It is difficult to cover all the manufactures of instruments and chemicals in this short article: it can be said that almost any analytical tools which have appeared in the literature are available in the domestic markets.

The Japan Analytical Instruments Manufacturers' Association was organized in 1960. At that time the annual gross output of analytical instruments was less than ten million U.S. dollars. However by 1970 it reached one hundred million dollars and one fifth was exported throughout the world.

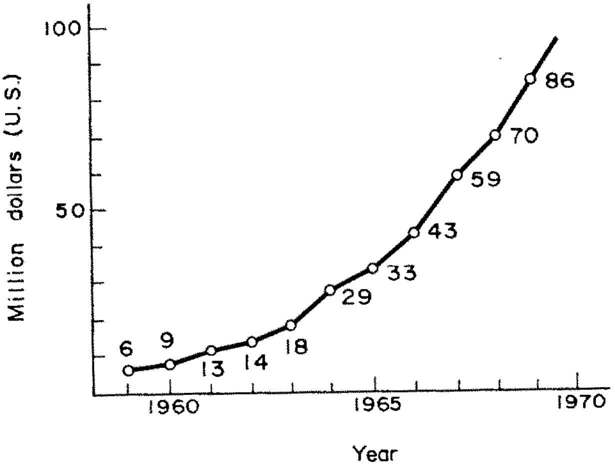


FIG 1.—Growth of Analytical Instrument Production.

TABLE I.—PRODUCTION AND EXPORT OF ANALYTICAL INSTRUMENTS (APRIL 1969–MARCH 1970)

	Output		Export	
Instruments	Amount*	%	Amount*	%
Electrochemical	5,534	6·6	267	1·8
Optical	25,307	30·0	5,183	33·0
Electromagnetic	22,736	26·9	7,475	47·5
Chromatographic	17,286	20·5	1,767	11·4
Distillation and separation	1,499	1·8	102	0·6
Thermometric	2,381	2·8	224	1·4
Miscellaneous	9,618	11·4	685	4·3
Total	84,362	100·0	15,730	100·0

* (Unit: US $1000).

Chemical societies

Finally, let me introduce briefly the Japan Society for Analytical Chemistry (JSAC), which celebrated its 20th anniversary last year. Most of the analytical chemists in Japan belong to the Chemical Society of Japan which was established about one hundred years ago, and some others to the Society of Agricultural Chemistry of Japan or the Pharmaceutical Society Japan as well as to the CSJ. After twenty years, the number of members of the JSAC exceeds 6,000; there are 31 honorary members, 850 company associates, 315 public members and 6,510 regular members. They publish their organ *Bunseki-Kagaku*, the "*Japan Analyst*", in Japanese with English abstracts every month, and the members and the subscribers receive the organ every month plus one annual review. Each issue carries an average of 20 original research papers. Altogether some 600 papers on analytical chemistry are published each year in Japanese journals. The JSAC holds one regular annual meeting and two local discussion meetings a year and at the annual meeting they grant the Society Prize to a few members who have contributed to the development of analytical chemistry and Progress Prizes to some promising young members. Besides these, they also award the Distinguished Service Prize to those who have served more than 25 years as chemical analysts in a company or research institute: the total number of D. S. Prize winners reached 710 in 1971. The JSAC has organized an International Congress on Analytical Chemistry in Kyoto in April, 1972 (from 3rd to 7th) sponsored by the International Union of Pure and Applied Chemistry, and the Science Council of Japan. Professor Em. Yuji Shibata, ex-president and member of the Japanese Academy of Science, who acted as the first President of the JSAC in 1951, is taking the presidentship of the International Congress. The Congress is hoped to be a fruitful meeting of 700 analytical chemists, including 300 overseas participants.

In conclusion, present-day Japan has been provided with all things abundantly, and it is not exceptional in the field of analytical chemistry either. However, it is most important now for the Japanese analytical chemists to make greater efforts to create new methodologies based on unique principles in order to contribute to analytical chemistry as a science as Mr. Utagawa described 145 years ago.

Talanta, 1972, Vol. 19, pp. 391 to 398. Pergamon Press. Printed in Northern Ireland

ION-SELECTIVE CHALCOGENIDE ELECTRODES FOR A NUMBER OF CATIONS

HIROSHI HIRATA and KENJI HIGASHIYAMA
Wireless Research Laboratory, Matsushita Electric Industrial Co. Ltd.
Kadoma, Osaka, Japan

(*Received* 7 *June* 1971. *Accepted* 2 *December* 1971)

Summary—Ion-selective chalcogenide disc electrodes have been developed which are responsive to cations such as silver, lead, chromium(III), nickel, cobalt(II), cadmium, zinc, copper(II) and manganese(II) ions. Each was prepared by using the corresponding metal chalcogenide with silver sulphide. An electrode was assembled with both a compacted and a sintered disc. The sintered electrodes were more sensitive and stable than the compacted ones. Response to silver ion was 59·5 mV/pAg, to lead, nickel, cadmium, zinc and copper(II) 29·5 mV/pM and to chromium(III) 20 mV/pM. Cobalt(II) and manganese(II) electrodes had a non-Nernstian response of 25 mV/pM. Both selenides and tellurides can be used for potentiometric determination, but the manganese(II) electrode serves as an analytical tool only when the disc consists of manganese(II) telluride and silver sulphide.

ION-SELECTIVE solid-state membrane electrodes have been developed for a number of cations and anions.[1] They may be classified into four main groups; single crystal membrane electrodes; compacted polycrystalline electrodes; heterogeneous membrane electrodes; glass electrodes. Strictly speaking, the sintered electrodes to be dealt with in the present paper belong to a fifth class.

A range of commercial solid-state membrane electrodes which respond to such cations as silver, copper(II) lead and cadmium has been introduced by Orion Research Inc. They are based on the corresponding metal sulphide with silver sulphide in the form of compacted discs.[1]

In our laboratory, a new type of ceramic electrode has been prepared by using sintering and hot-pressing methods; copper(I) sulphide ceramic electrode for copper(II),[2] lead sulphide–silver sulphide–copper(I) sulphide electrode for lead,[3] and cadmium sulphide–silver sulphide–copper(I) sulphide electrode for cadmium[4] have been developed in succession.

They proved to have several excellent characteristics, especially in their long-range stability and their reproducibility of response, and in their mechanical properties such as abrasion-resistance and breakage-strength.

Heterogeneous membrane electrodes for cations have also been developed in our laboratory; electrodes fabricated from silicone rubber membranes impregnated with copper(I) sulphide,[5] lead sulphide[6] and cadmium sulphide–silver sulphide.[7]

There are limitations in employing metal sulphides; the use of other sulphides is not possible because they are insufficiently conducting or are appreciably soluble in neutral and acidic solutions, or at least rather hygroscopic. Consequently, the use of metal chalcogenides other than sulphides has been investigated. As a result, metal chalcogenide electrodes were found to be applicable to a considerably wide variety of cations such as silver, lead, copper(II), cadmium, nickel, cobalt(II), manganese(II), zinc and chromium(III) ions.[8]

In this paper, the sensitivities of these disc electrodes are described.

EXPERIMENTAL

Apparatus

Measurements of e.m.f. to 0·1 mV were made on an Orion 801 pH-meter with the ion-selective electrode in conjunction with a double-junction reference electrode to prevent contamination from test solution.

Chemicals

Starting materials for preparing the electrodes, such as silver, lead, copper, nickel, cobalt, zinc, cadmium, manganese, chromium, sulphur, selenium and tellurium were commercially available and as pure as possible. All chemicals were analytical-reagent grade and used without further purification.

Stock metal in solutions (1*M*) were made by dissolving weighed amounts of the nitrates in distilled water, with no inert electrolytes added to maintain constant ionic strength, and diluted as required. All solutions were prepared from water which had been both demineralized and distilled.

Preparation of ceramic electrodes

Metal selenides or tellurides were prepared by the direct reaction of the elements in a high-vacuum sealed quartz tube. Silver sulphide, the carrier material, was obtained by direct reaction of silver with sulphur in a hydrogen sulphide gas stream.

A mixture of metal selenide (or telluride) and silver sulphide was compressed at a pressure of 10 ton/cm^2 to form a tablet with a diameter of 15 mm and a thickness of 2–3 mm, and then sintered at 100–600° for 3 hr in a stream of nitrogen.

Preparation of electrode

A cross-section of the electrode is shown in Fig. 1. The disc was fastened directly to a lead wire, and then mounted with epoxy resin adhesive in a stem of unbreakable epoxy resin which was highly resistant to acids, bases and organic solvents. An internal solution and an internal electrode were eliminated to avoid internal contamination and to simplify the structure of the electrode. The surface of the sintered disc was polished with diamond paste and washed with an ultrasonic cleaner.

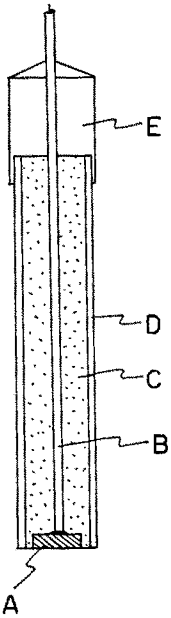


FIG. 1.—Cross-section of metal chalcogenide electrode.

A, Electrode disc
B, Lead wire
C, Insulator (epoxy resin)
D, Epoxy resin stem
E, Cap

Procedure

Potentiometric measurements were made in the conventional manner. The inner chamber of the double junction reference electrode was drained and filled once every two weeks, and the outer chamber was filled daily with saturated potassium nitrate solution. No potential changes were observed on filling. Between measurements, the electrode pair was rinsed several times with distilled water and wiped with filter paper. In the calibrations, the solutions were magnetically stirred at a constant, slow rate and readings were taken when equilibrium was reached (0·1–2 min).

RESULTS

Silver electrodes

Commercially available silver-selective electrodes contain a compacted disc of silver sulphide or a silicone rubber membrane impregnated with silver sulphide. The limit of detection may be restricted by the solubility of silver sulphide. Silver selenide and telluride are less soluble and therefore of potential use.

Figure 2 shows the potential *vs.* concentration curves of silver chalcogenide electrodes. The lower limit of the Nernstian slope is 10^{-7}–$10^{-8}M$ when silver selenide is used in place of the sulphide.[9]

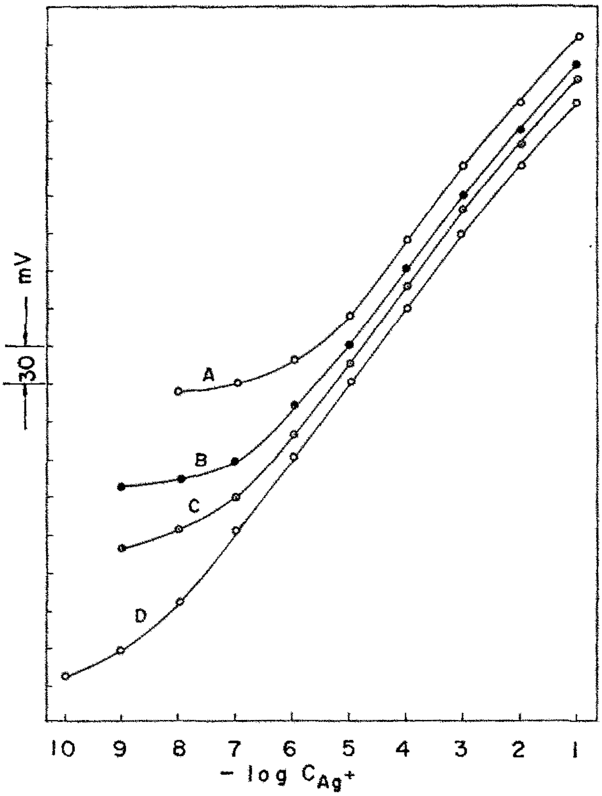


FIG. 2.—Potential responses of silver chalcogenide electrodes.

A. Compacted silver selenide
B. Sintered silver sulphide
C. Sintered silver telluride
D. Sintered silver selenide

The response rate of a silver selenide or telluride electrode is as fast as that of a sulphide one to $[Ag^+] > 10^{-6}M$, although the selenide or telluride has more covalent character than the sulphide. A ceramic chalcogenide electrode has better stability and reproducibility than a compacted one, and also better abrasion-resistance.

Other electrodes

The chalcogenides of the other metals investigated has to be mixed with silver sulphide in order to obtain electrodes that worked satisfactorily. These electrodes were compared with each other and with other membrane electrodes for the same elements. In general the metal sulphide electrodes were about as sensitive as commercial sulphide-type electrodes (which are usually made with a compacted mixture of metal sulphide and silver sulphide), and some orders of magnitude more sensitive than impregnated silicone-rubber electrodes. They also had better resistance to abrasion, had fast response, and gave stable and reproducible potentials.

Copper(I). The copper(I) selenide and telluride electrodes gave nearly the same performance as the sulphide electrode (which had the advantage that silver sulphide was not necessary for its functioning) with copper(II). The response slope was Nernstian down to $10^{-6}M$ copper(II) and the analytical range 10^{-8}–$10^{-1}M$.

Lead. The lead sulphide electrode gave Nernstian response down to $10^{-6}M$ lead, and so did the selenide and telluride electrodes, but the latter two gave a more sensitive response at lower concentrations than this. The response rates proved highly dependent on the nature of the active material, the composition of the disc and the temperature of sintering. The rate increased with lead chalcogenide content over the range 5–50%, and decreased if the sintering temperature was above the optimum of 300°.

Cadmium. Cadmium selenide electrodes behaved similarly to the sulphide electrodes, but the telluride electrode was superior both in linear response range and in sensitivity. The optimum composition was 10–50% w/w of chalcogenide, and the sintering temperature below 300° for a fast response to be obtained. Electrodes outside this range of composition were unsatisfactory. The response is Nernstian down to $10^{-6}M$.

Zinc. There was no commercial electrode available. Zinc orthophosphate and zinc sulphide were first tried as electrode materials but both were unsatisfactory for various reasons (drift, non-selectivity of the phosphate electrode) and this was attributed to the hygroscopic nature of these materials. The selenide and telluride were therefore tried and the selenide was found to give the best response if it was sintered with silver sulphide in a high-vacuum sealed quartz tube. The response is Nernstian down to $10^{-5}M$.

Manganese(II). Few investigations have been made of electrodes responsive to manganese(II). Buchanan and Seago[10] studied impregnated silicone-rubber electrodes and found that they were not selective; electrodes fabricated from membranes impregnated with manganese(II) carbonate and hydrogen phosphate trihydrate responded toward manganese(II) ion, but the presence of an additional electrolyte in the test solution levelled the response towards manganese(II) to that corresponding to the concentration of the added salt.

In the present study, manganese(II) chalcogenide disc electrodes were tried. However, manganese(II) sulphide could not be used, since it was very soluble in neutral and acidic solutions. Manganese(II) selenide mixed with silver sulphide was also moderately soluble in water and the surface became porous after several measurements, even when sintered. Consequently, only manganese(II) telluride could be used. Figure 3 shows the response of a manganese(II) telluride–silver sulphide disc sintered at 400°. This electrode exhibited fairly good response toward manganese(II) over the concentration range 10^{-1}–$10^{-5}M$ with an observed slope of 25 mV/pMn^{2+}. Moreover, there was no levelling effect from additional electrolytes such as alkali metal and alkaline earth metal ions in the test solution.

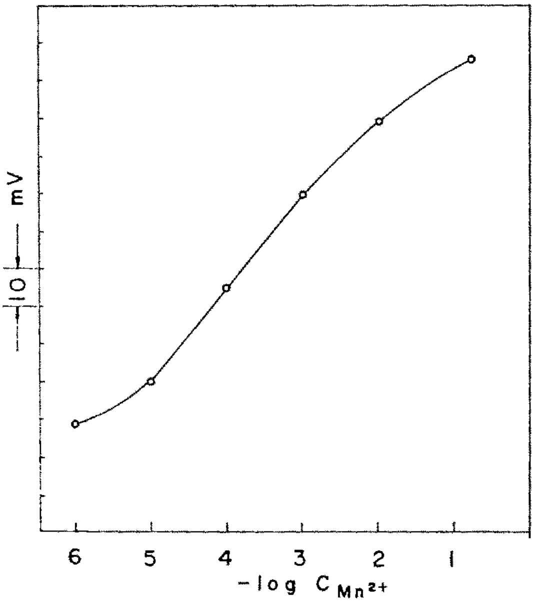


FIG. 3.—Potential response of sintered manganese(II) telluride electrode.

Chromium(III). No electrode has ever been studied which is responsive toward chromium(III), because of the lack of suitable active materials.

Chromium(III) selenide and telluride electrodes were studied, but did not respond rufficiently to chromium(III) ion, whether the chalcogenide was alone or incorporated with silver sulphide, in the form of compacted or sintered discs.

On the other hand, chromium(III) was found to interfere more or less for most of the cation-sensitive electrodes, the most remarkable interference being with a nickel selenide ceramic electrode. The potential *vs.* concentration curves for this electrode, as shown in Fig. 4, satisfies Nernst's law, but interferences from nickel by other ions which interfere with the potentiometric determination of nickel, cannot be avoided.

Cobalt(II). Few studies have been made on electrodes responsive to cobalt(II). Chatterjee[11] obtained a clay membrane that responded to copper(II), molybdenum, and cobalt(II). Buchanan and Seago[10] prepared a silicone-rubber membrane impregnated with cobalt(II) salts such as the carbonate and orthophosphate (octahydrate and anhydrous). These membranes, however, proved unsatisfactory, either by not giving the desired response or by having no selectivity toward cobalt(II).

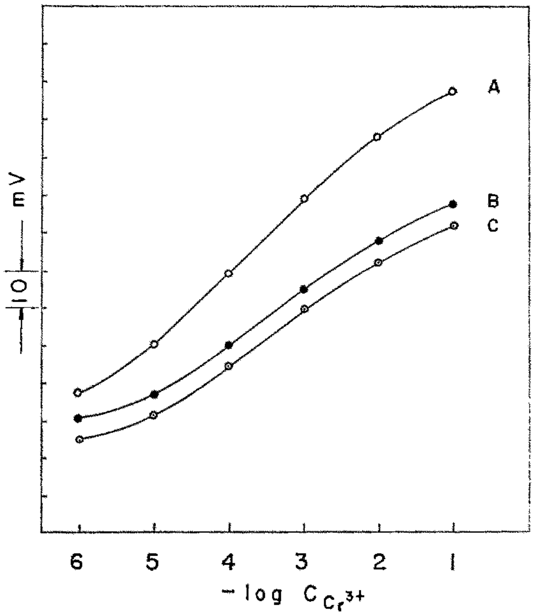


FIG. 4.—Potential responses of chromium(III) ion-sensitive electrodes.
A. Sintered nickel selenide
B. Sintered chromium(III) selenide
C. Sintered chromium(III) telluride

Cobalt(II) sulphide was found here to show no response toward cobalt(II). Cobalt(II) selenide added to silver sulphide and sintered in an inert gas stream responded nicely to cobalt(II), but compacted cobalt(II) selenide or telluride and sintered cobalt(II) telluride electrodes, proved unsatisfactory (Fig. 5).

The response characteristics seem highly dependent on the nature of the chalcogenide and silver sulphide, the temperature and time of sintering, and the inert gas used in the sintering.

Nickel. Several electrodes responsive toward nickel have been investigated. Morazzani-Pelletier and Baffier[12] studied collodion and paraffin membranes embedded with nickel salts. Buchanan and Seago[10] prepared silicone-rubber membranes impregnated with nickel dimethylglyoximate, nickel acetylacetonate (dihydrate and anhydrous), nickel carbonate and nickel orthophosphate heptahydrate. Dobbelstein and Diehl[13] investigated membranes of collodion, of epoxy polyester, and of phenol-formaldehyde, containing nickel dimethylglyoximate, and a membrane prepared by polymerizing phenol, formaldehyde, ammonia and nickel nitrate.

Only membrane electrodes impregnated with nickel salts, and not chelates, responded towards nickel ion, but were non-selective.

Nickel sulphide electrodes were found by us to be so poor in response to nickel that after several measurements they no longer responded properly. Nickel selenide and telluride, however, gave sensitive and selective response to nickel, which were linear over the range 10^{-5}–$10^{-1}M$, with a slope of 29·5 mV. The sintered disc gave a more Nernstian response than a compacted one did.

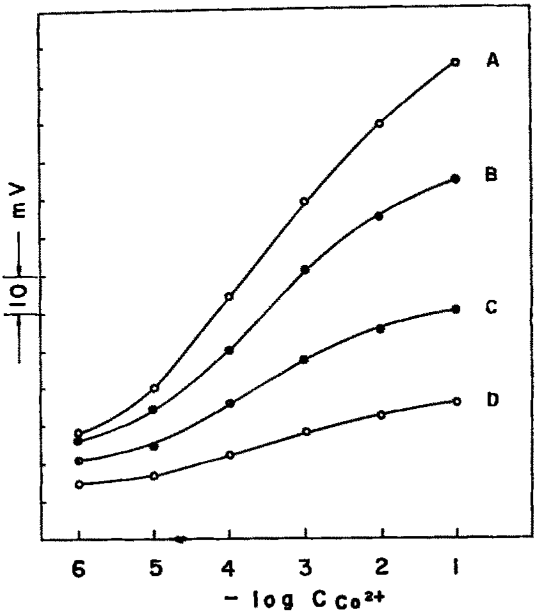


FIG. 5.—Potential responses of cobalt(II) chalcogenide electrodes.
A. Sintered cobalt(II) selenide
B. Sintered cobalt(II) telluride
C. Compacted cobalt(II) selenide
D. Compacted cobalt(II) telluride

The response rates varied with composition and the temperature of sintering. Among the common ions, silver, copper(II), mercury(II), iron(III), sulphide and chloride interfered seriously. But over 1000-fold amounts of alkali metal, alkaline earth metal, aluminium, zinc, cadmium, cobalt, manganese(II) and nitrate did not interfere at all. At constant ionic strength, the potentials did not change over a pH range from below zero to the pH at which nickel hydroxide precipitated. The discs showed Nernstian slopes at temperatures from 0° to 95°.

DISCUSSION

The mechanism of the response by a mixed crystalline electrode is not so well understood as that of a single crystal or a liquid ion-exchanger membrane electrode. Up to the present, the behaviour of these electrodes has been explained on the basis of ion-exchange occurring at the interface between electrode and solution, plus some mechanisms for conduction through the bulk of the electrode disc. Recently Brand and Rechnitz[14] made impedance measurements on mixed crystalline electrodes such as the lead-selective electrode, which has a compacted disc containing a mixture of lead sulphide and silver sulphide. As a result, charge was found to build up at the membrane–solution interface, producing a capacitative effect. However, it is very difficult, in terms of only the capacitative effect, to explain the role played by the silver sulphide.

Most metal sulphides other than silver sulphide can only be used as active material if mixed with the latter. For example, a highly-purified lead sulphide electrode, in which no traces of silver could be detected by qualitative emission spectroanalysis, proved non-responsive toward lead, whereas, an impure lead sulphide electrode containing trace amounts of silver was much more sensitive than a pure one. Cadmium sulphide behaves similarly, and it seems that silver sulphide must be incorporated in both compacted and sintered electrodes.

As seen in this paper, a number of metal selenides and tellurides, when incorporated with silver sulphide, function in a similar manner to sulphide electrodes.

From the experimental results, it seems that particular silver ions arising from imperfections in the crystal lattice play a predominant role in ion-selective solid-state electrodes. The presence of silver ions, especially interstitial ones, renders the disc conductive and capable of providing sensitivity, fast response and the other response characteristics suitable for potentiometric measurements.

Acknowledgement—The authors thank Dr. S. Kisaka, Dr. K. Sugihara, Dr. S. Hayakawa and Dr. S. Mori for their encouragement in this work.

Zusammenfassung—Es wurden ionenselektive Scheibenelektroden aus Chalkogeniden entwickelt, die auf Kationen wie Silber, Blei, Chrom(III), Nickel, Kobalt(II), Cadmium, Zink, Kupfer(II) und Mangan(II) ansprechen. Jede Elektrode wurde sowohl mit einer gepreßten als auch mit einer gesinterten Scheibe aufgebaut. Die gesinterten Elektroden waren empfindlicher und stabiler als die gepreßten. Die Elektroden sprechen auf Silber mit 59,5 mV/pAg, auf Blei, Nickel, Cadmium, Zink und Kupfer(II) mit 29,5 mV/pM und auf Chrom(III) mit 20 mV/pM an. Kobalt(II)- und Mangan(II)-Elektroden gehorchten der Nernstschen Beziehung nicht und zeigten 25 mV/pM. Sowohl Selenide als auch Telluride konnen zur potentiometrischen Bestimmung verwendet werden; die Manganelektrode ist jedoch analytisch nur dann nutzbar, wenn die Scheibe aus Mangan(II)-tellurid und Silbersulfid besteht.

Résumé—On a mis au point des électrodes de chalcogénure sélectives aux ions, qui répondent à des cations tels que les ions argent, plomb, chrome(III), nickel, cobalt(II), cadmium, zinc, cuivre(II) et manganèse(II). On a préparé chacune d'elles en utilisant le chalcogénure métallique correspondant avec le sulfure d'argent. On a assemblé l'électrode avec un disque aggloméré ou fritté. Les électrodes frittées sont plus sensibles et stables que les électrodes compactes. La réponse est de 59,5 mV/pAg pour l'ion argent, de 29,5 mV/pM pour les plomb, nickel, cadmium, zinc et cuivre(II), et de 20 mV/pM pour le chrome(III). Les électrodes de cobalt(II) et manganèse(II) ont une réponse non-Nernstienne de 25 mV/pM. On peut utiliser tant les séléniures que les tellurures pour le dosage potentiométrique, mais l'électrode de manganèse(II) ne sert comme outil analytique que lorsque le disque est constitué de tellurure de manganèse(II) et de sulfure d'argent.

REFERENCES

1. R. A. Durst (Editor), *Ion-Selective Electrodes*, N.B.S. Spec. Publ. 348, U.S. Printing Office, Washington, 1970.
2. H. Hirata, K. Higashiyama and K. Date, *Anal. Chim. Acta*, 1970, **51**, 209.
3. H. Hirata and K. Higashiyama, *Anal. Chim. Acta*, 1971, **54**, 415; *Bull. Chem. Soc. Japan*, 1971, **44**, 2420.
4. *Idem*, Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.
5. H. Hirata and K. Date, *Talanta*, 1970, **17**, 883.
6. *Idem*, *Anal. Chem.*, 1971, **43**, 297.
7. *Idem*, to be published.
8. H. Hirata and K. Higashiyama, Patent pending.
9. R. A. Durst and B. T. Duhart, *Anal. Chem.*, 1970, **42**, 1002.
10. E. B. Buchanan, Jr., and J. L. Seago, *ibid.*, 1968, **40**, 517.
11. B. Chatterjee and D. K. Mitra, *J. Indian Chem. Soc.*, 1955, **32**, 751.
12. S. Morazzani-Pelletier and M. A. Baffier, *J. Chim. Phys.*, 1965, **62**, 429.
13. T. N. Dobbelstein and H. Diehl, *Talanta*, 1969, **16**, 1341.
14. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1970, **42**, 478.

Talanta, 1972, Vol. 19, pp. 399 to 406. Pergamon Press. Printed in Northern Ireland

STALAGMOMETRIC TITRATIONS

TOMIHITO KAMBARA and TOMOE KIBA
Department of Chemistry, Faculty of Science, Hokkaido
University, Sapporo, Japan

(*Received* 7 *June* 1971. *Accepted* 19 *October* 1971)

Summary—End-point detection in some precipitation titrations is achieved by measurement of the surface tension between mercury and the solution ("stalagmometric" titration). The drop-time of a polarographic dropping mercury electrode in open circuit is plotted against volume of surface-active titrant added, and shows a break or a peak at the end-point. The stalagmometric titration of sodium tetraphenylborate with Zephiramine (tetradecyldimethylbenzylammonium chloride) was satisfactory and made possible the determination of potassium by back-titration. Potassium was also titrated directly with tetraphenylborate and with calcium dipicrylaminate. Sodium dodecylbenzenesulphonate was titrated directly with Zephiramine and the results were compared with those obtained by the *p*-toluidine method and Epton's method.

ACCORDING to Kolthoff and Stenger,[1] the "stalagmometric" method of end-point detection was applied as far back as 1841 by Clark to the determination of water hardness, with a soap solution as the titrant. At that time, the end-point was detected by observing the appearance of foaming of the solution. Then the stalagmometer was introduced by Traube[2] in 1914. Later, the capillary–manometric method[3] and also the ring method[4] were employed for surface tension measurements, and some investigations on acid-base titrations with long-chain fatty acids or certain alkaloids have been reported.

Very little has been done in this field recently, presumably because of the lack of a convenient and suitable method of surface tension measurement.

The authors have developed an interfacial tensiometric titration method, based on measurement of the drop-time for a dropping mercury electrode immersed in the solution being titrated (stalagmometric titration). The drop-time gives an approximate relative value of surface tension between mercury and the solution according to Tate's law.

EXPERIMENTAL

Reagents

Sodium tetraphenylborate.

Zephiramine. (Tetradecyldimethylbenzylammonium chloride; Zeph-Cl).

Potassium chloride standard solution. Potassium chloride (reagent grade), dried for 3 hr in air at 110°, was used.

Calcium dipicrylaminate $Ca[N\{C_6H_2(NO_2)_3\}_2]_2$.

Sodium dodecylbenzenesulphonate.

Water. Distilled and demineralized.

Apparatus

Dropping mercury capillary. The capillary characteristics at 0·50-m mercury column height were: $m = 0{\cdot}839_4$ mg/sec and $t = 17{\cdot}0_7$ sec in pure water at 21·6°. The electrode was used in open circuit.

Measurement of the drop time. A stop-watch readable to 0.1 sec was used.

General procedure

Figure 1 shows the assembly used for the stalagmometric titration. The titrant is added to the beaker from the burette as usual, and the solution in the beaker is stirred and allowed to stand for a while after each addition. The time for five mercury drops to fall is measured with a stop-watch, and a further volume of titrant is added. A plot of drop-time against volume of titrant added gives the stalagmometric titration curve. The point of the maximum drop-time is taken as the end-point.

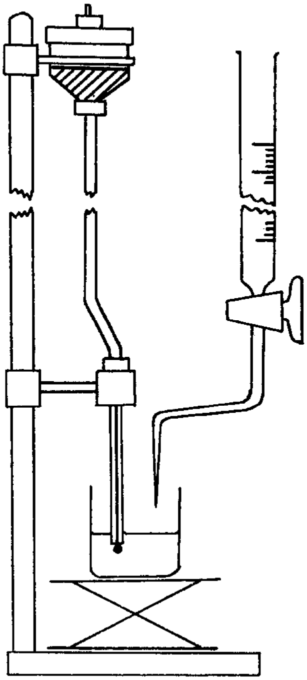


FIG. 1.—Assembly used for the stalagmometric titration.

RESULTS AND DISCUSSION

Titration of sodium tetraphenylborate with Zephiramine

Sodium tetraphenylborate reacts stoichiometrically with Zeph-Cl, forming a white precipitate. Bromophenol Blue or Titan Yellow as adsorption indicator has been used in this reaction for the indirect determination of potassium.[5-7]

In the present work, the relationship between the surface tension and the concentration of these reagents has been studied. Series of solutions of both $Na(C_6H_5)_4B$ and Zeph-Cl covering the concentration range from $10^{-6}M$ to $10^{-2}M$ in $10^{-3}M$ sodium chloride were prepared. The drop-time for each solution was measured and plotted against the logarithm of the concentration. Figure 2 clearly indicates that both of these reagents are surface-active.

The titration curves for the stalagmometric titration of $Na(C_6H_5)_4B$ with Zeph-Cl are shown in Fig. 3. A sharp peak, *i.e.*, a sudden increase in surface tension, was seen in each curve, and was taken as the end-point. This new method was compared with the ordinary Bromophenol Blue method (adsorption indicator),[5] and the results are given in Table I. By the familiar *F*- and *t*-tests, it has been confirmed that there is no significant difference between the variances and means of these two groups of results.

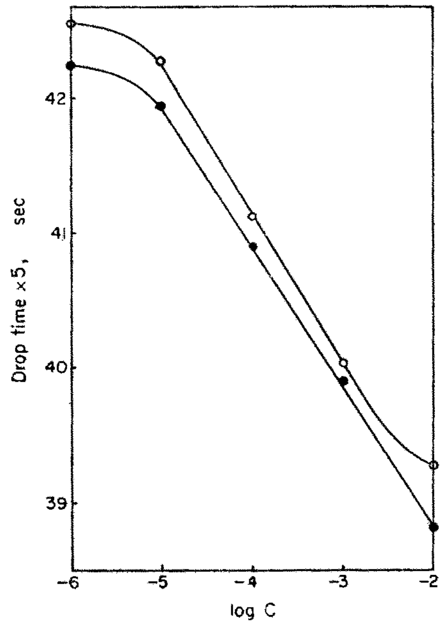


FIG. 2.—Change of drop-time of the dropping mercury capillary with the concentration *C* of surface-active substance.

Open circle Zeph-Cl; closed circle $Na(Ph)_4B$; environment (supporting electrolyte or blank solution) $10^{-3}M$ NaCl.

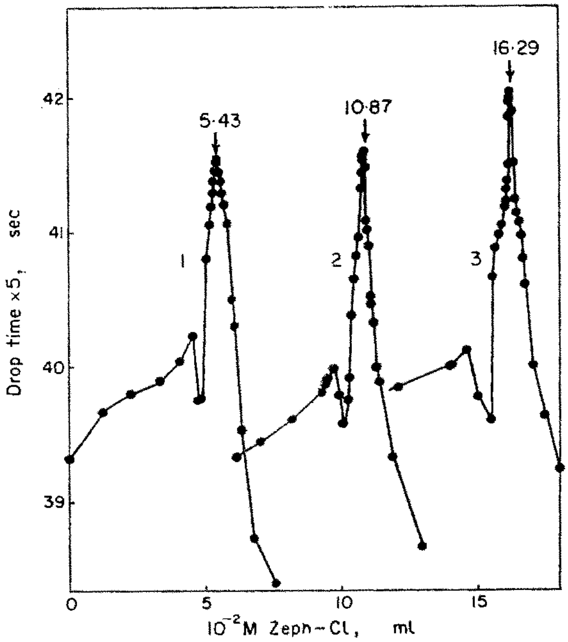


FIG. 3.—Stalagmometric titration curves of $Na(Ph)_4B$ with $10^{-2}M$ Zeph-Cl solution. $10^{-2}M$ $Na(Ph)_4B$ solution taken: (1) 5·00 ml; (2) 10·00 ml; (3) 15·00 ml.

TABLE I.—RESULTS OF TITRATIONS

Titration	Titrant volume used for 5-ml of sample solution, and its standard deviation, *ml*	Number of titrations
$10^{-2}M$ $Na(C_6H_5)_4B$ with $10^{-2}M$ Zeph-Cl		
by stalagmometric method	$5{\cdot}42_9 \pm 0{\cdot}00_4$	6
by BPB method	$5{\cdot}43_0 \pm 0{\cdot}01_0$	3
$10^{-1}M$ KCl with $10^{-1}M$ $Na(C_6H_5)_4B$		
by stalagmometric method	$4{\cdot}94_8 \pm 0{\cdot}02_0$	7
calculated value*	$4{\cdot}93_5 \pm 0{\cdot}01_4$	3
$10^{-2}M$ KCl with $10^{-2}F$ Ca-dipicrylaminate		
by stalagmometric method	$2{\cdot}47_7 \pm 0{\cdot}00_4$	9

* Calculated from the factor of the $Na(C_6H_5)_4B$ solution which was standardized against the standard Zeph-Cl solution by the Bromophenol Blue method.

Back-titration of potassium

A known volume of $10^{-2}M$ aqueous potassium solution was transferred to a 25-ml volumetric flask, a known excess of $Na(C_6H_5)_4B$ solution was added, and the flask was filled up to the mark with water. The white precipitate was allowed to stand in contact with the mother liquor for some time before being separated by filtration. A 20-ml portion of the filtrate was titrated stalagmometrically with $10^{-2}M$ Zeph-Cl. Titration curves similar to those in Fig. 3 were obtained, and complete recovery of potassium from potassium chloride was achieved.

Direct titration of potassium with sodium tetraphenylborate

The direct titration of potassium with $Na(C_6H_5)_4B$ is an interesting problem and has been realized through the use of various techniques including conductometric,[8] potentiometric,[9] amperometric[10] and high-frequency measurements.[11]

The solubility product of the salt being not so small ($pK_{sp} = 7{\cdot}7$), $0{\cdot}1M$ solutions were used, the $0{\cdot}1M$ tetraphenylborate solution being standardized by the Bromophenol Blue method against standard $10^{-2}M$ Zeph-Cl. A few examples of the titration curves obtained by the direct titration are given in Fig. 4. Only one component is surface-active, so the titration curve shows quite a different shape from those in Fig. 3. Satisfactory results were obtained, as summarized in Table I.

Direct titration of potassium with calcium dipicrylaminate

Dipicrylaminate, which forms a sparingly soluble salt with potassium ion, has been used for the separation and gravimetric determination of potassium. The mercury drop-time was plotted against the logarithm of the concentration (Fig. 5), showing that dipicrylaminate is remarkably surface-active.

The direct stalagmometric titration of potassium was tried with $10^{-2}M$ calcium dipicrylaminate solution as titrant. Some titration curves are reproduced in Fig. 6, and the results in Table I.

Titration of sodium dodecylbenzenesulphonate with Zephiramine

The anionic surfactant Na-DBS may be titrated with $10^{-2}M$ Zeph-Cl by the stalagmometric method.[12] In the present study, Zeph-Cl was titrated with $10^{-2}M$ Na-DBS solution (Fig. 7). As would be expected from the fact that both components are surface-active agents, the plot has a sharp peak at the equivalence point.

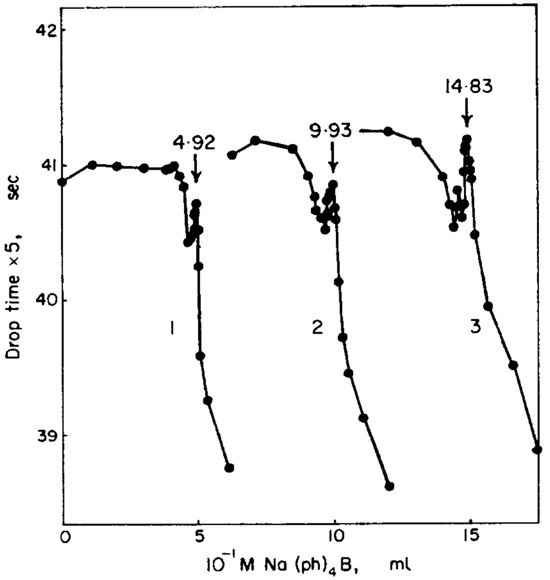


FIG. 4.—Stalagmometric titration curves of KCl with $10^{-1}M$ Na(Ph)$_4$B solution. $10^{-1}M$ KCl solution taken: (1) 5·00 ml; (2) 10·00 ml; (3) 15·00 ml.

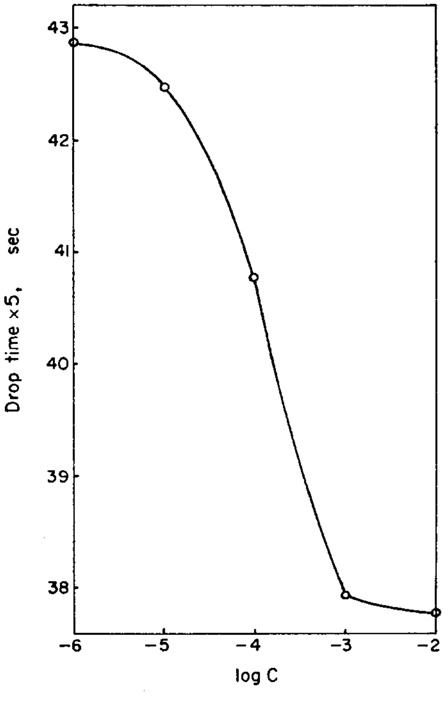


FIG. 5.—Change of drop-time of the dropping mercury capillary with the concentration C of calcium dipicrylaminate in $10^{-3}M$ NaCl environment.

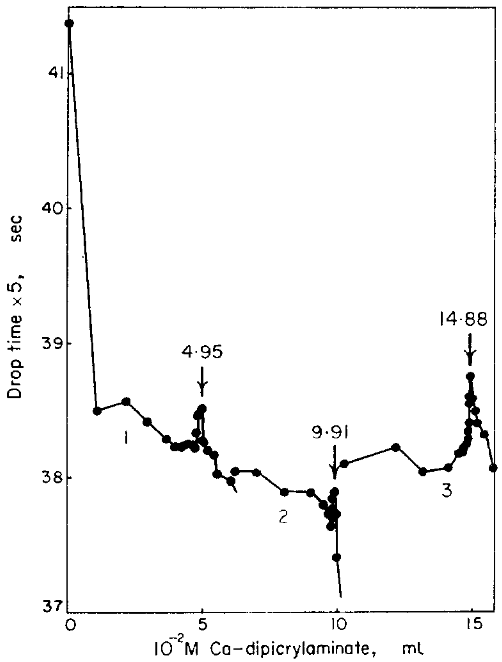


FIG. 6.—Stalagmometric titration curves of KCl with $10^{-2}M$ calcium dipicrylaminate solution.
$10^{-2}M$ KCl solution taken: (1) 5·00 ml; (2) 10·00 ml; (3) 15·00 ml.

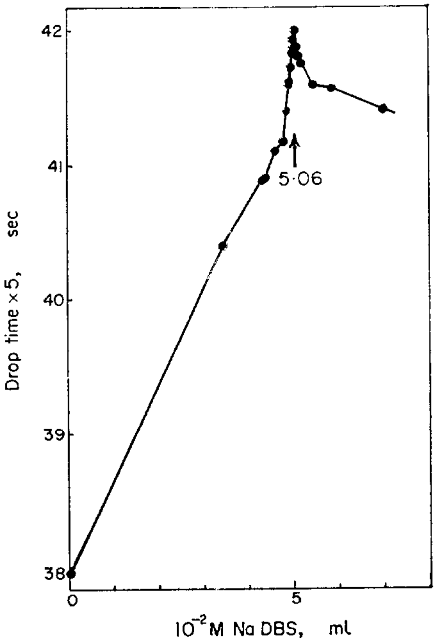


FIG. 7.—Stalagmometric titration curve of Zeph-Cl with $10^{-2}M$ Na-DBS solution.
$10^{-2}M$ Zeph-Cl solution taken: 5·00 ml.

TABLE II.—DETERMINATION OF Na-DBS CONTENT

Method	Na-DBS content found, %	Number of determinations
Stalagmometric titration	$90{\cdot}3_8 \pm 0{\cdot}2_0$	9
p-Toluidine method	$90{\cdot}2_1 \pm 0{\cdot}2_1$	3
Epton's method	$92{\cdot}7_2 \pm 0{\cdot}3_8$	3

In Table II, the content of Na-DBS obtained from the stalagmometric titration is compared with that from the *p*-toluidine method, *i.e.*, the Wickbold method,[13] in which the toluidinium salt is extracted into ether and titrated with standard sodium hydroxide solution. There is no significant difference between the variances and means of these two sets of results.

By Epton's method,[14] *i.e.*, two-phase titration with quaternary ammonium salt, with Methylene Blue as indicator, the Na-DBS content was found to be about 2% higher than these values.

Zusammenfassung—Die Endpunktsbestimmung in einigen Fällungstitrationen wird durch Messung der Oberflächenspannung zwischen Quecksilber und der Lösung bewerkstelligt ("stalagmometrische" Titration). Die Tropfzeit einer polarographischen Quecksilbertropfelektrode bei offenem Stromkreis wird gegen das Volumen des zugegebenen oberflächenaktiven Titranten aufgetragen; sie zeigt beim Endpunkt einen Knick oder eine Spitze. Die stalagmometrische Titration von Natriumtetraphenyloborat mit Zephiramin (Tetradecyl-dimethyl-benzyl-ammoniumchlorid) war zufriedenstellend und ermöglichte die Bestimmung von Kalium durch Rücktitration. Kalium wurde auch direkt mit Tetraphenyloborat und Calciumdipikrylaminat titriert. Natrium-dodecylbenzolsulfonat wurde direkt mit Zephiramin titriert und die Ergebnisse mit denen der p-Toluidinmethode und des Verfahrens nach Epton verglichen.

Résumé—La détection du point de fin de dosage dans certains titrages par précipitation est réalisée par la mesure de la tension superficielle entre du mercure et la solution (titrage "stalagmométrique"). Le temps de goutte d'une électrode polarographique à goutte de mercure en circuit ouvert est tracé en fonction du volume d'agent de titrage tensio-actif ajouté, et montre une brisure ou un pic au point de fin de dosage. Le titrage stalagmométrique du tétraphénylborate de sodium par la Zephiramine (chlorure de tétradécyldiméthylbenzylammonium) est satisfaisant et rend possible le dosage de potassium par titrage en retour. On a aussi dosé le potassium directement par le tétraphénylborate et par le dipicrylaminate de calcium. On a titré le dodécylbenzène sulfonate de sodium directement par la Zéphiramine et les résultats ont été comparés à ceux obtenus par la méthode à la *p*- toluidine et la méthode d'Epton.

REFERENCES

1. I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2nd Ed., Vol. 1, pp. 274–8. Interscience, New York, 1942.
2. I. Traube and R. Somogyi, *Intern. Z. Physik. Chem. Biol.*, 1914, **1**, 479.
3. A. B. Taubmann, *Z. Physik. Chem.*, 1932, **A161**, 141.
4. A. Lottermoser and E. Schladitz, *Kolloid Z.*, 1933, **64**, 44.
5. E. D. Schall, *Anal. Chem.*, 1957, **29**, 1044.
6. E. M. Epps and J. C. Burden, *ibid.*, 1958, **30**, 1882.
7. T. Iwachido, *Talanta*, 1966, **13**, 1697.

8. G. Jander and A. Anke, *Z. Anal. Chem.*, 1957, **154**, 8.
9. K. Kilsson, W. J. Kirsten and A. Berggren, *Anal. Chem.*, 1958, **30**, 237.
10. W. R. Amos and R. F. Sympson, *ibid.*, 1959, **31**, 133.
11. E. S. Lane, *Analyst*, 1957, **82**, 406.
12. T. Kambara, T. Kiba, K. Saitoh and M. Ohshima, *Bunseki Kagaku*, 1971, **20**, 365.
13. I. Nishi, T. Imai and M. Kasai, *Handbook of Surface Active Agents* (*Kaimen-Kasseizai Binran*), p. 818. Sangyo Tosho Publishing Co., Tokyo, 1960.
14. *Idem*, *ibid.*, p. 811, p. 831.

Talanta, 1972, Vol. 19, pp. 407 to 414. Pergamon Press. Printed in Northern Ireland

INVESTIGATION OF MANGANESE(III) FLUORIDE FOR COULOMETRIC TITRATION

M. KATOH and T. YOSHIMORI
Faculty of Engineering, Science University of Tokyo, Shinjuku-ku, Tokyo, Japan

(*Received* 19 *June* 1971. *Accepted* 30 *August* 1971)

Summary—A study has been made of the use of electrogenerated manganese(III), in an electrolyte containing fluoride, for coulometric titration. The addition of fluoride prevented the deposition of manganese dioxide on the anode, and was responsible for increase of the current efficiency and for extension of the feasible range of current density, owing to complex formation between manganese(III) and fluoride. The bonding ratio, the apparent stability constant and the redox potential of the complex were also estimated from the Nernst equation and the current-potential curves.

SEVERAL investigations[1–4] have been reported dealing with the generation of manganese(III) for coulometric titration. The electrolytes used mainly consisted of manganese(II) sulphate and sulphuric acid, sometimes with phosphoric acid added. In the present study, potassium fluoride was also added to the electrolyte and a distinct improvement was found.

Tutundžić first used manganese(II) sulphate solution as the electrolyte for coulometric oxidimetry.[1] He considered the anodically oxidized product in the electrolyte to be permanganate. Subsequent investigators,[2–4] however, pointed out that manganese(III) was the most likely species to be produced. One of the disadvantages of these procedures was the formation of manganese dioxide on the anode surface. Although the earlier authors did not refer to the phenomenon, the current efficiency at the anode should be diminished by the formation of the dioxide. The other problem was the small current feasible, which was less than 40 $\mu A/mm^2$ under optimum conditions [$0{\cdot}2M$ manganese(II) sulphate and 2–$7M$ sulphuric acid].

Manganese(III) forms several complexes. The fluoride,[5] metaphosphate[6] and pyrophosphate[7] complexes have already been used in the determination of this element. It may therefore be expected that these anions can be used to prevent the deposition of manganese dioxide on the anode, and may also raise the upper limit of the current density for the electrogeneration of the oxidant.

In the present study, the formation of manganese dioxide has been found to be largely prevented by addition of potassium fluoride to the electrolyte, and the limiting current density has been increased several fold.

Meta- and pyrophosphates are not considered here, because metaphosphate sometimes produces precipitates with tervalent cations, and the pyrophosphate complex is not stable in acidic media. The mechanism of the reaction has also been elucidated, by interpretation of the absorption spectra and the current–potential curves for the generator electrode. The composition and stability of the fluoromanganese(III) complex are also deduced from the potential variations of the indicator electrode with time during a constant-current electrolysis.

EXPERIMENTAL

Apparatus

Cell and electrodes. The main electrolysis cell consisted of two tall-form lipless beakers. They were used for an anolyte and for a catholyte, and were connected by means of a saturated potassium sulphate agar-agar bridge. Both beakers were fitted with silicone rubber stoppers. The reference electrode of Hg–Hg_2SO_4–H_2SO_4 (0·615 V *vs.* N.H.E. at 25°) was joined to the anolyte cell, through an intermediate beaker containing 1*N* sulphuric acid, with the same kind of sulphate bridges as just described. A platinum plate (200 mm^2) was used as a cathode. An anode (generator electrode) consisting of a platinum plate (250 mm^2), an indicator electrode made of a platinized platinum plate (250 mm^2) and a nitrogen inlet were set in the anolyte cell. An electronic constant-current source (d.c.) was used for the electrolysis. When a resistance inserted between the output terminals of this supply was changed from 0 to 100 ohm, the variation of the current was 0·6 mA at 220 mA and 0·17 mA at 100 mA. The stability of the current was ±0·01 % during 60 min. The current was measured from the *IR* drop across a standard series resistor (100 ohm ± 0·01 %) by using a precision potentiometer. The potential between the reference electrode and the anode or the indicator electrode was measured with an electronic potentiometer (Yokokawa Electric Co. Tupe PM-20). The time of the electrolysis was measured with a stop-clock having a synchronous motor.

Reagents

Sulphuric acid, (1*N*, 55 ml), was used for both the intermediate solution and the catholyte. Two electrolytes (55 ml) were generally used as the anolyte: *A*, 0·5*M* manganese(II) sulphate–1*N* sulphuric acid; *B*, 0·5*M* manganese(II) sulphate–1*N* sulphuric acid–0·1–0·5*M* potassium fluoride. All electrolytes were prepared from chemicals of analytical grade. Before the electrolysis the anolyte was deaerated by passage of purified nitrogen for half an hour. The temperature of the electrolyte was maintained at 25° by a thermostat.

RESULTS AND DISCUSSION

Behaviour of the anode during the electrolysis

During the electrolysis of anolyte *A*, which contained no fluoride, a brownish black deposit was formed on the anode surface irrespective of the current density applied. The deposit is presumed to be manganese dioxide because the Pourbaix diagram[8] shows stable regions of MnO_2 (between 1·16 and 1·67 V *vs.* N.H.E. near pH 0·3, corresponding to our experimental conditions). Outside this region, manganese(II) on the less noble and permanganate on the more noble side are shown to be stable species. When anolyte *B*, which was more than 0·1*M* in fluoride was used, no deposit was formed on the electrode.

The formation of manganese dioxide on the anode may cause serious difficulties in the coulometric titration. As the electricity will be partly consumed for formation of this compound, the current efficiency may be decreased. On this basis addition of fluoride was considered to be effective for obtaining higher current efficiency. Further study, therefore, was directed to identify the anodic products from *A* and *B*.

Absorption spectra of the anolyte after electrolysis

In order to identify the products of the anode, absorption spectra were measured. A standard solution of manganese(III) was prepared by the following method.[9] A solution that was 0·2*M* in manganese(II) sulphate, 0·05*M* in potassium permanganate and 0·6*M* in sulphuric acid was allowed to stand for a day, then filtered, and the absorption spectrum of the filtrate was measured.

A solution that was 1m*M* in potassium permanganate and 1*N* in sulphuric acid was used as the standard permanganate solution. Both spectra are shown in Fig. 1, and are almost the same as those reported by Lingane *et al.*[2]

Solution *A* was electrolysed at 2·50 mA for 1800 sec. The spectrum of the anolyte after the electrolysis is also shown in Fig. 1. The spectrum was identical with that

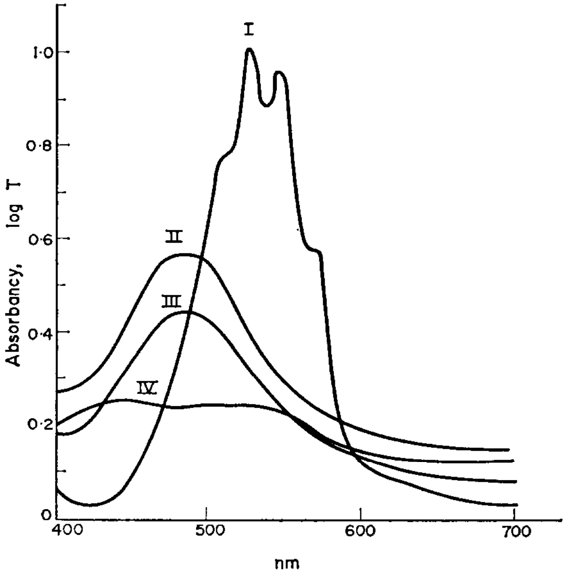


FIG. 1.—Absorption spectra
[I] : 1m*M* $KMnO_4$.
[II] : 0·56 m*M* Mn^{3+}.
[III] : Solution A after electrolysis for 1800 sec at 2·5 mA.
[IV] : Solution B (0·1*M* KF) after electrolysis for 1800 sec at 2·5 mA.

of manganese(III), showing the anodically oxidized product was not permanganate but manganese(III). In this case manganese dioxide was also formed on the anode.

The absorption spectrum of solution *B*(0·1*M* fluoride) after electrolysis under the same conditions was quite different from that of permanganate or manganese(III). This indicates that a manganese(III) fluoride complex may be formed in the solution.

Both solutions were then electrolysed for various time intervals at constant current (2·50 mA). The results obtained are shown in Fig. 2.

The curve for solution *A* was slightly convex, which indicated that the formation of

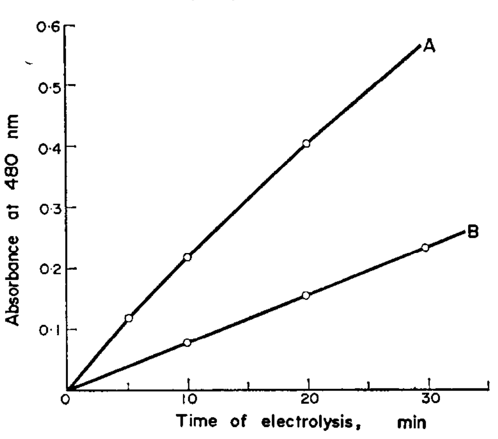


FIG. 2.—Increase of the absorbance as a function of the time of electrolysis
A : Solution *A*
B : Solution *B* (0·1*M* KF)

manganese dioxide on the anode would be slower in the initial stages of the electrolysis than in the later ones. This phenomenon is probably due to the formation of manganese dioxide. In the case of the solution *B*, on the other hand, strict proportionality was observed between the time of the electrolysis and the concentration of manganese(III) fluoride complex.

Further study on the fluoro-manganese(III) complex

Solution *A* and four types of solution *B* which differed in potassium fluoride concentration were anodically oxidized for 600 sec at 2·5 mA, while being stirred magnetically at constant rate. After cessation of the current, the stirring was continued for an additional 40 min. The potentials of the indicator electrode (platinized platinum) were measured every minute during these 50 min. The platinized platinum electrode was preferable to smooth platinum foil because of its good response. Figure 3 shows the results of the measurements. The potential became almost constant within 5 min after cessation of the current in all cases.

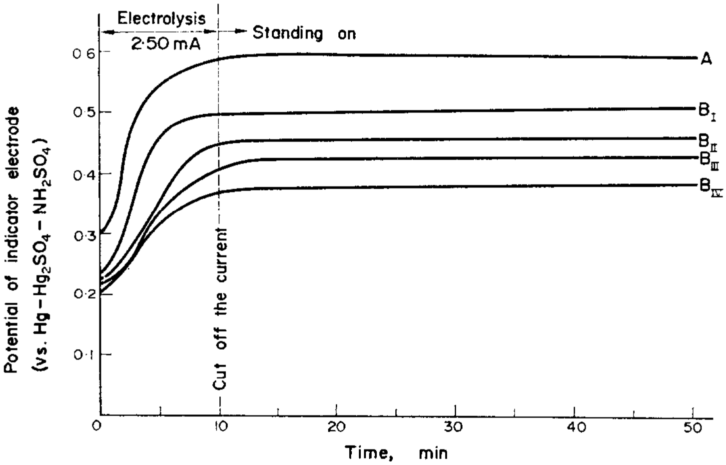


FIG. 3.—Build-up of the potential and the response of the indicator electrode.
A; Solution *A*:
B$_{I}$; Solution *B* (0·1*M* KF): B$_{II}$; Solution *B* (0·2*M* KF):
B$_{III}$; Solution *B* (0·3*M* KF): B$_{IV}$; Solution *B* (0·5*M* KF).

The results of Fig. 3 were interpreted as follows. The complex-formation reaction is given by equation (1).

$$\mathrm{Mn}^{3+} + x\mathrm{HF} \rightarrow \mathrm{MnF}_x^{3-x} + x\mathrm{H}^+ \tag{1}$$

The stability constant is

$$K = [\mathrm{MnF}_x^{3-x}][\mathrm{H}^+]^x/[\mathrm{Mn}^{3+}][\mathrm{HF}]^x \tag{2}$$

Although each term should be an activity, molar concentrations were used for convenience. Therefore *K* is the apparent stability constant.

Mass balance for manganese(III) gives equation (3).

$$[\mathrm{Mn}^{3+}] + [\mathrm{MnF}_x^{3-x}] = C \tag{3}$$

where C is the total concentration of manganese(III). Substituting (3) into (2), we obtain

$$K = \{C - [\mathrm{Mn}^{3+}]\}[\mathrm{H}^+]^x/[\mathrm{Mn}^{3+}][\mathrm{HF}]^x \tag{4}$$

In (4), $[\mathrm{Mn}^{3+}]$ can be obtained from the following relationship at 25°:

$$E = E^\circ + 0{\cdot}059 \log [\mathrm{Mn}^{3+}]/\mathrm{Mn}^{2+}] \tag{5}$$

where $[\mathrm{Mn}^{2+}]$ is almost constant because the concentration of manganese(III) formed by the electrolysis is only $2{\cdot}83 \times 10^{-4}M$ and is negligibly small compared with the total concentration of manganese(II) ($0{\cdot}5M$). E° is known to be 1·50 V *vs.* N.H.E. and E can be determined from Fig. 3. The term $C - [\mathrm{Mn}^{3+}]$ in equation (4) is nearly equal to C provided that the fluoro-manganese(III) complex is very stable. Such an assumption is reasonable because of the spectra (Fig. 1, curves III and IV) and this is confirmed by the high stability constant obtained later. Hence (4) can be rearranged as follows:

$$\log [\mathrm{Mn}^{3+}] - \log C = -\log K - x\{\log [\mathrm{HF}] + \mathrm{pH}\} \tag{6}$$

where $[\mathrm{Mn}^{3+}]$ can be obtained from (5) and C is calculated from the number of coulombs passed (and found to be $2{\cdot}83 \times 10^{-4}M$). The left-hand side of (6) can be designated q. In the right-hand side of (6), the pH was calculated to be about 0·3, from the dissociation constants of sulphuric acid, $k_1 = \infty$ and $k_2 = 1{\cdot}3 \times 10^{-2}$ at 25°. The next problem is the estimation of [HF]. The following equilibria exist in the solution B:

$$[\mathrm{H}^+][\mathrm{F}^-]/[\mathrm{HF}] = k_1 \tag{7}$$

$$[\mathrm{HF}_2{}^-]/[\mathrm{HF}][\mathrm{F}^-] = k_2 \tag{8}$$

$$2[\mathrm{HF}_2{}^-] + [\mathrm{HF}] + [\mathrm{F}^-] + x[\mathrm{MnF}_x^{3-x}] = C' \tag{9}$$

where C' represents the total concentration of fluoride; k_1 and k_2 are given[10] as $6{\cdot}71 \times 10^{-4}$ and 3·86 respectively, at 25°. In this case $x[\mathrm{MnF}_x^{3-x}]$ is again neglected owing to its negligibly small concentration. According to the relationships (7), (8) and (9), HF was the main species at present pH 0·3. $[\mathrm{HF}_2{}^-]$ and $[\mathrm{F}^-]$ can then be neglected, to a first approximation, and [HF] equated with C'. Therefore plots of q against $\{\log [\mathrm{HF}] + \mathrm{pH}\}$ are possible from the values of Fig. 3, the potentials for use in (5) being the values 30 min after the current had been cut off. The resultant straight line gave x and $\log K$ from the slope and intercept respectively, $x = 3{\cdot}0$ and $\log K = 5{\cdot}1$ being obtained. This means that the composition of the complex is MnF_3, under the experimental conditions used, and the stability is moderately high even in such a strongly acidic solution. The value of $\log K$ is only an apparent value because activity coefficients were ignored, but serves as an estimate of the stability. The formal redox potential for equation (10) may also be calculated from this value.

$$\mathrm{MnF}_3 + 3\mathrm{H}^+ + e \rightleftharpoons \mathrm{Mn}^{2+} + 3\mathrm{HF} \tag{10}$$

$$E^\circ = 1{\cdot}20\ \mathrm{V}\ vs.\ \mathrm{N.H.E.}$$

This couple is apparently less noble than that of equation (11),

$$\mathrm{Mn}^{3+} + e \rightleftharpoons \mathrm{Mn}^{2+} \tag{11}$$

$$E^\circ = 1{\cdot}50\ \mathrm{V}\ vs.\ \mathrm{N.H.E.}$$

Since the standard redox potential of (10) is almost the same as that of (12) below, no interaction will occur between the two, that is, no manganese dioxide is formed.

$$\begin{gathered} MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \\ E^\circ = 1{\cdot}23 \text{ V } vs. \text{ N.H.E.} \end{gathered} \tag{12}$$

In the absence of potassium fluoride, the following disproportionation reaction will occur:

$$2Mn^{3+} + 2H_2O \rightarrow MnO_2 + Mn^{2+} + 4H^+ \tag{13}$$

This was confirmed in the present experiment.

Anodic behaviour

The anodic polarization curves of solutions *A* and *B* were measured from the stepwise increase of the electrolytic current. In this experiment, only a small amount of manganese(III) is formed in the first period of the electrolysis. This causes, however, an appreciable potential change in the solution, and disturbs the measurements of the potential of the anode. Therefore the electrolyte (*A* or *B*) was pre-electrolyzed for 15 min at a current of 2·5 mA before the first measurement of the potential. The pregenerated manganese(III) depressed the appreciable change of the equilibrium potential of the solution, as can be predicted from the Nernst equation. Thus, the over-potential of the anode could be obtained more easily.

The limiting currents were observed by this method, and are shown in curves *A*, B_1, B_2 and B_3 of Fig. 4. The curve for solution *A* is nearly the same as the results obtained previously.[2,3,11] We consider that the currents in solutions *A* and *B* are limited by the kinetics and not by a diffusion process. The biamperometric titration

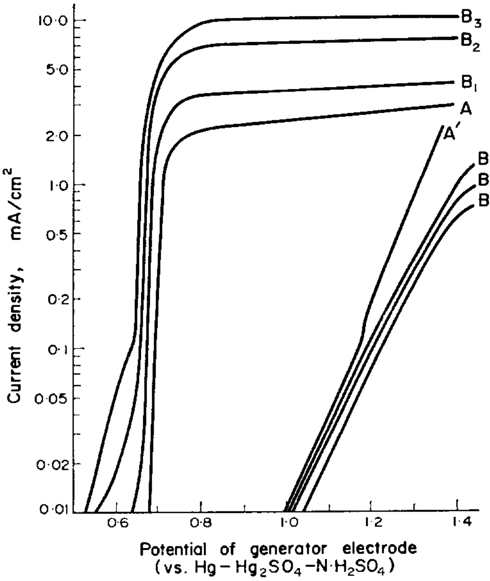


FIG. 4.—Anodic polarization curves in various electroyltes
A; Solution *A*: B_1; Solution *B* (0·1*M* KF):
B_2; Solution *B* (0·3*M* KF): B_3; Solution *B* (0·5*M* KF).
A′–B_3′: Solutions *A*–B_3 without manganese(II).

curve of iron(II) with this electrolyte also indicated the irreversibility of this electrode reaction. The results will be shown in the next report.

Lingane *et al.*[3] concluded from their chronopotentiometric study that the anodic process is kinetically controlled. T. Sekine *et al.*[8] also derived the same explanation from the activation energy (38·5 kJ/mole) for this process, which is higher than that for a diffusion process. It is interesting to note that the limiting current increases linearly with increase of fluoride concentration. When the concentration of sulphuric acid in solution *B* (0·5*M* fluoride) was increased to 6*N*, the current density was further increased (up to 0·15 mA/mm^2).,

In Fig. 4 the curves marked with a "dashed" letter were measured for solutions without manganese(II) sulphate. The current efficiency for the generation of manganese(III) was calculated from the difference of the currents at the same potential with and without manganese(II). It is assumed that the current consumed in the absence of manganese will also be consumed in addition to that required to oxidize manganese(II) when the latter is present. The efficiencies are shown in Fig. 5. It can be concluded from these curves that a higher current density for generation of manganese(III) is obtained in the fluoride-containing solutions; *i.e.*, the feasible range of current is wider when fluoride is present than when it is absent.

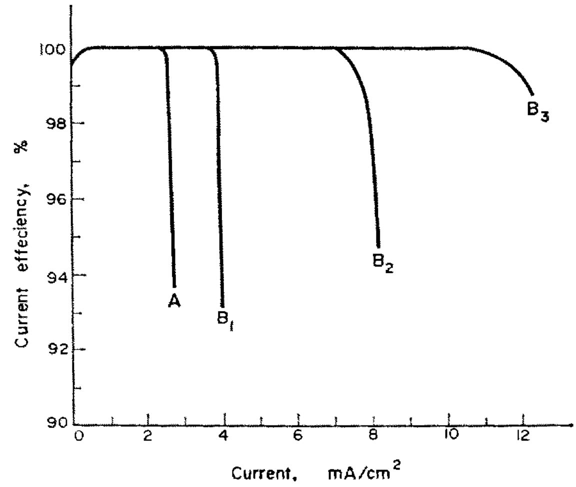


FIG. 5.—Current efficiencies estimated from the anodic polarization curves
A; Solution *A*: B_1; Solution *B* (0·1*M* KF):
B_2; Solution *B* (0·3*M* KF): B_3; Solution *B* (0·5*M* KF).

Acknowledgement—The authors wish to thank Mr. T. Shibuya and Mr. K. Shimizu for their assistance in the experiments.

Zusammenfassung—Die Verwendung von elektrolytisch in einem fluoridhaltigen Elektrolyten erzeugtem Mangan(III) zur coulometrischen Titration wurde untersucht. Die Zugabe von Fluorid verhinderte durch Komplexbildung mit Mangan(III) die Abscheidung von Mangandioxid an der Anode und ergab eine Erhöhung der Stromausbeute sowie eine Ausdehnung des nutzbaren Stromdichtebereichs. Das Bindungsverhältnis, die scheinbare Bildungskonstante und das Redoxpotential des Komplexes wurden aus der Nernstschen Gleichung und aus den Stromspannungskurven berechnet.

Résumé—On a effectué une étude sur l'emploi du manganèse(III) électrogénéré, dans un électrolyte contenant du fluorure, pour le titrage coulométrique. L'addition de fluorure prévient le dépôt de bioxyde de manganèse sur l'anode et est responsable de l'accroissement de l'efficacité du courant et de l'extension du domaine praticable de densité de courant, du fait de la formation de complexe entre le manganèse(III) et le fluorure. Le taux de liaison, la constante de stabilité apparente et le potentiel redox du complexe ont aussi été estimés à partir de l'équation de Nernst et des courbes courant-potentiel.

REFERENCES

1. T. Tutundžić and S. Mladenović, *Anal. Chim. Acta*, 1955, **12**, 382.
2. R. G. Selim and J. J. Lingane, *ibid.*, 1959, **21**, 536.
3. A. J. Fenton and N. H. Furman, *Anal. Chem.*, 1960, **32**, 748.
4. R. P. Buck, *ibid.*, 1963, **35**, 692.
5. R. Lang and F. Kurtz, *Z. Anorg. Allgem. Chem.*, 1929, **181**, 111.
6. R. Lang, *Z. Anal. Chem.*, 1935, **102**, 8.
7. J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 191.
8. M. Pourbaix, *Atlas of Electrochemical Equilibrium in Aqueous Solutions*, p. 290, Pergamon, Oxford, 1966.
9. K. J. Vetter and G. Manecke, *Z. Physik. Chem. Leipzig*, 1950, **195**, 270.
10. W. M. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, p. 52. Prentice-Hall, New York, 1964.
11. T. Sekine and M. Sugimori, *J. Electrochem. Soc. Japan*, 1969, **37**, 63.

Talanta, 1972, Vol. 19, pp. 415 to 422. Pergamon Press. Printed in Northern Ireland

SOLVENT EXTRACTION OF ANIONS WITH METAL CHELATE CATIONS—XVIII*

SPECTROPHOTOMETRIC DETERMINATION OF MALEIC ACID IN THE PRESENCE OF FUMARIC ACID BY SOLVENT EXTRACTION WITH TRIS(1,10-PHENANTHROLINE)IRON(II) CHELATE CATIONS

Y. YAMAMOTO, T. KUMAMARU and M. MURANAKA
Department of Chemistry, Faculty of Science, Hiroshima University
Higashisenda, Hiroshima, Japan

(*Received* 14 *June* 1971. *Accepted* 29 *August* 1971)

Summary—A new colorimetric method is proposed for the determination of maleic acid. Among aliphatic dicarboxylic acids tested, maleic acid was found to be selectively extracted into nitrobenzene as the red ion-association complex (λ_{max} 516 nm) formed between the hydrogen maleate anion and the tris(1,10-phenanthroline)iron(II) cation. At least a 32-fold molar excess of tris(1,10-phenanthroline)iron(II) relative to maleic acid is needed and the optimal pH range is 3–5. A linear relationship is obtained over the concentration range 10^{-5}–10^{-4} M maleic acid. The relative standard deviation was 1·0%. The colour intensity of the extract remains constant at room temperature for at least 24 hr. A large amount of fumaric acid, the *trans*-isomer of maleic acid, is not extracted under the same conditions. This makes it possible to determine maleic acid in the presence of fumaric acid.

MALEIC ACID or maleic anhydride is one of the important raw materials for industrial production of polyester resins, alkyd resins, *etc.* Several procedures for the determination of maleic acid have been published, especially regarding the separation from fumaric acid. Markman and Chikryzova[1] presented a simultaneous determination of maleic acid and fumaric acid by polarography with 0·1M hydrochloric acid in 90% ethanol as a supporting electrolyte. Funasaka *et al.*[2] proposed an ultraviolet spectrophotometric method combined with a salting-out chromatographic separation from fumaric acid, but the procedure seems to be somewhat tedious. Burger and Schulek[3] devised a new titrimetric method for the determination of maleic acid and fumaric acid, using bromine monochloride and mercury(II), and Kreshkov *et al.*[4] reported on the analysis of mixtures of 2 or 3 dicarboxylic acids by potentiometric titration in non-aqueous solution.

In our previous papers of this series, certain aromatic organic acids such as pentachlorophenol,[5,6] picric acid[7] and phthalic acid,[8,9] the structures of which are relatively symmetrical, were found to be selectively extracted into particular organic solvents with cationic metal chelates such as tris(1,10-phenanthroline)iron(II), tris(2,2′-bipyridyl)iron(II), bis(cuproine)copper(I) or bis(neocuproine)copper(I). Such extraction systems have been successfully utilized for the spectrophotometric determination of the organic acids. In connection with these investigations, we also studied the extraction behaviour of various aliphatic dicarboxylic acids, and found

---

* Part XVII: T. Kumamaru, Y. Hayashi, N. Okamoto, E. Tao and Y. Yamamoto, *Anal. Chim. Acta*, 1966, **35**, 524.

that among them maleic acid can also be selectively extracted into nitrobenzene with tris(1,10-phenanthroline)iron(II). This work was undertaken in order to establish a new colorimetric method for the determination of maleic acid in the presence of fumaric acid. The method has the advantage of being not only sensitive and accurate but also free from interference by the organic acid homologues.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water.

Standard maleic acid solution, $2{\cdot}5 \times 10^{-4}M$.

Other carboxylic acid solutions, $2{\cdot}5 \times 10^{-4}M$. Stock solutions ($0{\cdot}01M$) of these acids (adipic, crotonic, fumaric, glutaric, DL-malic, malonic, oxalic, succinic and L-tartaric) were diluted as required before use.

Tris(1,10-phenanthroline)iron(II) sulphate solution, $1{\cdot}6 \times 10^{-2}M$. Prepared by dissolving 6·343 g of 1,10-phenanthroline monohydrate and 3·187 g of ferrous ammonium sulphate hexahydrate in dilute sulphuric acid and diluting the mixture to 500 ml with water. The resulting solution (pH 3·5) is $1{\cdot}6 \times 10^{-4}M$ in tris(1,10-phenanthroline)iron(II) sulphate and $1{\cdot}6 \times 10^{-4}M$ with respect to excess of 1,10-phenanthroline.

Buffer solution. The phosphate buffers for pH 4–9 were prepared by mixing $0{\cdot}3M$ potassium dihydrogen phosphate and $0{\cdot}3M$ disodium hydrogen phosphate in suitable ratios. More acidic or alkaline solutions were prepared by mixing $0{\cdot}3M$ potassium dihydrogen phosphate with $0{\cdot}5M$ sulphuric acid, or $0{\cdot}3M$ disodium hydrogen phosphate with $0{\cdot}5M$ sodium hydroxide.

General procedure

Transfer by pipette into a 100-ml separating funnel 5 ml of a carboxylic acid solution ($2{\cdot}5 \times 10^{-4}M$), 5 ml of the phosphate buffer solution and 5 ml of the tris(1,10-phenanthroline)iron(II) sulphate solution ($1{\cdot}6 \times 10^{-2}M$). Dilute the mixture to 25 ml with water and add 10 ml of nitrobenzene. Shake the funnel for 1 min with a mechanical shaker. After 30 min, transfer the nitrobenzene extract to a 15-ml glass tube with a stopper and dry it with 1 g of anhydrous sodium sulphate. Measure the absorbance at 516 nm, using a reagent blank extract or nitrobenzene as a reference.

Recommended procedure for the determination of maleic acid

Calibration curve. Transfer by pipette into 100-ml separating funnels 0–10 ml of the standard maleic acid solution ($2{\cdot}5 \times 10^{-4}M$) and 5 ml of pH 3·5 phosphate buffer solution, and then proceed as for the general procedure.

Determinations. Proceed as above, taking an amount of sample containing no more than 7 mg of maleic acid in a total volume less than 15 ml.

RESULTS AND DISCUSSION

Extraction behaviour of aliphatic dicarboxylic acid homologues

Absorption spectra. Figure 1 shows the visible absorption spectra of the extracts from the pH 3·5 phosphate-buffered solutions which contained maleic acid or one of its homologues. The presence of maleic acid leads to a considerable increase in the absorbance; malonic acid is slightly extracted and gives a similar absorption spectrum. These spectra are characterized by the absorbance maximum at 516 nm.

pH study. Figure 2 shows the influence of pH on the degree of extraction of maleic acid and malonic acid from the phosphate-buffered solutions. The absorbance of the extract from a solution of maleic acid is maximal and constant if the pH of the aqueous phase is 3–5. The degree of the extraction of malonic acid is fairly low and the other seven dicarboxylic acids mentioned above are not scarcely extracted at all under the same conditions.

The distribution curves for maleic acid species (calculated from $\mathrm{p}K_{a_1}$ 1·92, $\mathrm{p}K_{a_2}$ 6·22)[10] indicate that the hydrogen maleate anion predominates in pH range 3–6

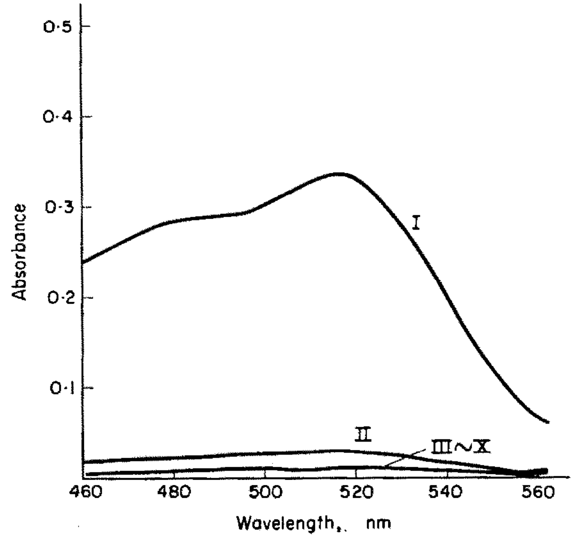


FIG. 1.—Absorption spectra of nitrobenzene extracts.
Organic phase, 10 ml; aqueous phase, 25 ml [$Fe(phen)_3$ 3·2 × $10^{-8}M$, dicarboxylic acid 1·0 × $10^{-4}M$, pH 3·5]; reference, nitrobenzene. (I) Maleic acid, (II) malonic acid, (III) DL-malic acid, (IV) fumaric acid, (V) oxalic acid, (VI) succinic acid, (VII) glutaric acid, (VIII) adipic acid, (IX) L-tartaric acid, (X) reagent blank.

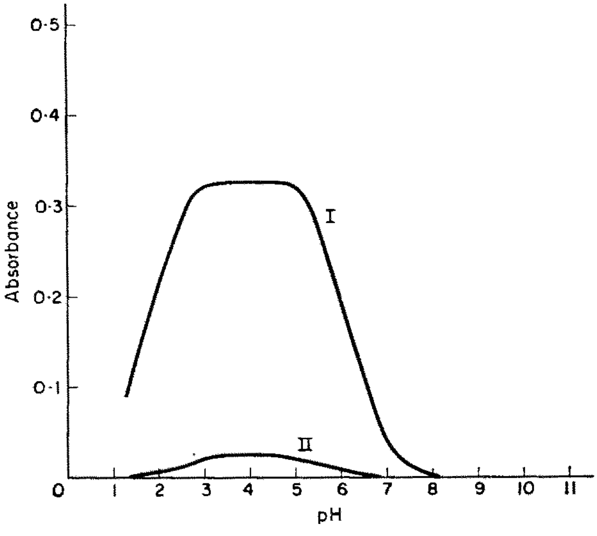


FIG. 2.—Effect of pH on the extraction of maleic acid and malonic acid.
Dicarboxylic acid, 1·0 × $10^{-4}M$; reference, reagent blank. (I) Maleic acid, (II) malonic acid.

(Fig. 3); it is probable that this singly-charged anion participates in the extraction. A possible reason for the specificity of the extraction of maleic acid is the formation by this anion of a seven-membered symmetric ring through an intramolecular hydrogen bond, which results in good charge distribution and a lower hydration energy. In order to confirm the composition of the extracted species, continuous

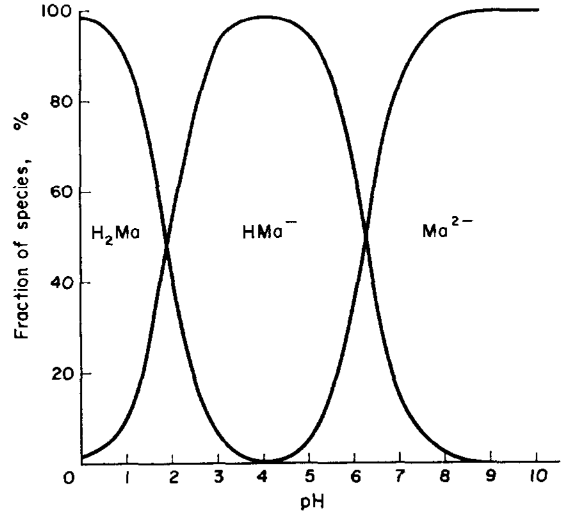


FIG. 3.—Distribution of maleate species as a function of pH: H_2Ma = maleic acid.

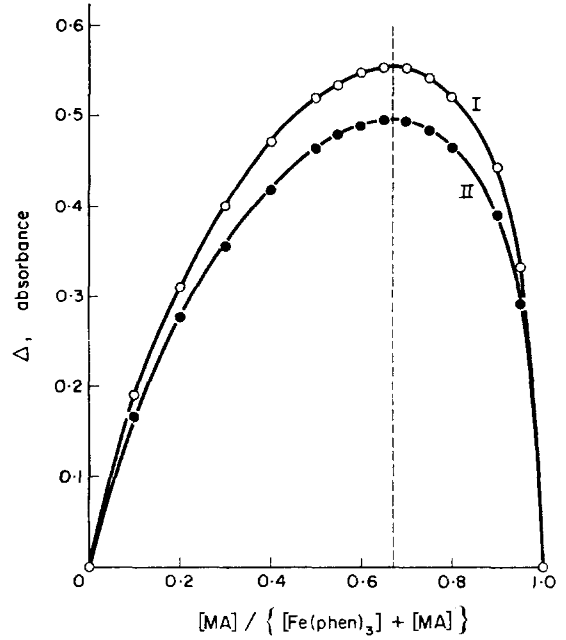


FIG. 4.—Continuous variation plots for phenanthroline–iron(II) hydrogen maleate at pH 3·5.
[Fe(phen)$_3$] + [MA], 8·0 × 10^{-4}*M*; reference, reagent blank. (I) 516 nm, (II) 490 nm.
MA = maleic acid.

variation plots for maleic acid were made, at wavelengths of 490 and 516 nm. As shown in Fig. 4, the maximum absorbance occurred at a ratio of *ca.* 0·65. This fact together with the result of the pH study suggests that a 1:2 ion association complex is formed between the tris(1,10-phenanthroline)iron(II) cation and the hydrogen maleate anion, and is transferred into nitrobenzene.

It is of interest that fumaric acid, the *trans*-isomer of maleic acid, is not extracted even in the pH range 3·5–4, where the hydrogen fumarate anion is predominant (Fig. 5). This behaviour may be accounted for as follows. The charge distribution on the singly-charged anion may be assumed to be localized, because of the lack of hydrogen-bonding, and the resultant selective hydration may be strong enough to prevent the ion-association complex from forming.

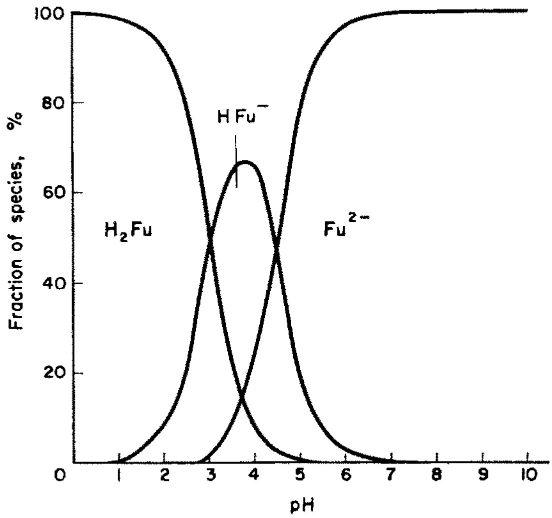


FIG. 5.—Distribution of fumarate species as a function of pH: H_2Fu = fumaric acid.

Development of analytical method for maleic acid

By utilization of the selective solvent extraction of tris(1,10-phenanthroline)iron(II) hydrogen maleate, it may be possible to determine maleic acid colorimetrically.

Effect of reagent concentration. With other variables constant, different amounts of tris(1,10-phenanthroline)iron(II) sulphate were added to an aqueous solution of maleic acid and extraction was done as described above. To obtain the maximum colour response it was found necessary to maintain a minimum 32-fold molar excess of the tris(1,10-phenanthroline)iron(II) cation relative to maleic acid. Therefore, the chelate concentration was usually kept at $3{\cdot}2 \times 10^{-3}M$ and the maximum maleic acid concentration at $10^{-4}M$. Large amounts of the pH 3·5 phosphate buffer solution are without deleterious effect.

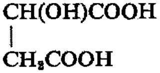
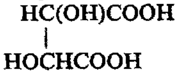
Effect of shaking time. The shaking time for the extraction was varied from 0·5 to 10 min, while the other variables were kept constant. Extraction was quantitative with 15 sec of shaking. Continued shaking up to 10 min produced no further change of absorbance.

Colour stability of the extracts. Extractions were made on a series of maleic acid solutions in the usual way, after which the absorbances were measured as a function of time. The colour intensity of the extracts remained almost constant for at least 24 hr under normal laboratory conditions. This extraction system is negligibly affected by temperature over the range tested, 15–30°.

Calibration curve and precision. The recommended procedure for the calibration curve was established on the basis of the results above. The calibration curve was found to be linear over the concentration range 1–10 × $10^{-5}M$ maleic acid in the initial aqueous phase. Under these conditions, 29 μg of maleic acid give an absorbance of 0·033 in a 10-mm cell and at 516 nm, when extracted into 10 ml of nitrobenzene. The precision was estimated from ten results for 1·0 × $10^{-4}M$ maleic acid. The mean absorbance was 0·326 with a standard deviation of $0{\cdot}003_4$ (relative standard deviation 1·0%).

Effect of diverse substances. The influence of diverse substances on the extraction was studied under experimental conditions similar to those used for the calibration curve. The tolerance for a given substance was defined as the maximum concentration which could be present without causing a deviation of about 0·01 in the absorbance of the extract from 1·0 × $10^{-4}M$ maleic acid. Tolerances for several maleic acid homologues are listed in Table I. Large amounts of sulphate, phosphate, carbonate, fluoride, and moderate amounts of chloride and nitrate did not interfere. Interference of larger amounts of chloride, bromide or iodide could be eliminated by precipitation with silver sulphate. Nitrite should be decomposed by boiling with sulphamic acid. Metal ions interfere only if they form relatively stable maleate complexes, but can be masked by addition of non-interfering stronger complexing agents such as EDTA.[11–14]

TABLE I.—EFFECT OF MALEIC ACID HOMOLOGUES

Substance		Tolerance, $10^{-4}M$
Fumaric acid	 $\begin{array}{c}\text{HCCOOH}\\ \|\\ \text{HOOCCH}\end{array}$	100
Oxalic acid	 $\begin{array}{l}\text{COOH}\\ \vert\\ \text{COOH}\end{array}$	5
Malonic acid	$\text{HOOCCH}_2\text{COOH}$	0·5
Succinic acid	$\text{HOOC(CH}_2)_2\text{COOH}$	25
Glutaric acid	$\text{HOOC(CH}_2)_3\text{COOH}$	100
Adipic acid	$\text{HOOC(CH}_2)_4\text{COOH}$	100
DL-Malic acid	 $\begin{array}{l}\text{CH(OH)COOH}\\ \vert\\ \text{CH}_2\text{COOH}\end{array}$	5
L-Tartaric acid	 $\begin{array}{c}\text{HC(OH)COOH}\\ \vert\\ \text{HOCHCOOH}\end{array}$	100
Crotonic acid	 $\begin{array}{c}\text{H}_3\text{CCH}\\ \|\\ \text{HCCOOH}\end{array}$	25

Maleic acid taken: 1·0 × $10^{-4}M$.

Application of the method. To make sure that maleic acid could be determined in the presence of fumaric acid, the procedure was applied to known sample solutions containing both isomers in various ratios. The results obtained are summarized in Table II.

The fumaric acid has a negligible effect on the absorbance. Thus maleic acid can be determined in the presence of fumaric acid.

TABLE II.—DETERMINATION OF MALEIC ACID IN THE PRESENCE OF FUMARIC ACID

[MA]/[FA]*	[MA], $10^{-4}M$		Recovery of MA, %
	taken	found	
25/75	0·40	$0{\cdot}40_2$	$100{\cdot}_5$
	0·60	$0{\cdot}60_3$	$100{\cdot}_5$
	0·80	$0{\cdot}79_7$	$99{\cdot}_6$
	1·00	$0{\cdot}99_3$	$99{\cdot}_3$
50/50	0·40	$0{\cdot}39_8$	$99{\cdot}_5$
	0·60	$0{\cdot}60_1$	$100{\cdot}_2$
	0·80	$0{\cdot}79_4$	$99{\cdot}_3$
	1·00	$1{\cdot}00_3$	$100{\cdot}_3$
75/25	0·40	$0{\cdot}40_2$	$100{\cdot}_4$
	0·60	$0{\cdot}60_6$	$101{\cdot}_0$
	0·80	$0{\cdot}80_8$	$101{\cdot}_0$
	1·00	$1{\cdot}00_0$	$100{\cdot}_0$

* Ratio of maleic acid to fumaric acid.

Zusammenfassung—Eine neue kolorimetrische Methode zur Bestimmung von Maleinsäure wird vorgeschlagen. Unter den geprüften aliphatischen Dicarbonsäuren wird nur Maleinsäure selektiv als rotes Ionenassoziat (λ_{max} 516 nm) aus Hydrogenmaleat und Tris(1,10-phenanthrolin)eisen(II) in Nitrobenzol extrahiert. Man braucht mindestens einen 32-fachen molaren Überschuß an Tris(1,10-phenanthrolin)eisen(II) über Maleinsäure; der optimale pH-Bereich ist 3–5. Eine lineare Beziehung findet man bei 10^{-5}–$10^{-4}M$ Maleinsäure. Die relative Standardabweichung beträgt 1,0%. Die Farbintensität des Extrakts bleibt bei Raumtemperatur mindestens 24 h stabil. Eine große Menge von Fumarsäure, dem trans-Isomeren der Maleinsäure, wird unter den selben Bedingungen nicht extrahiert. Damit wird es möglich, Maleinsäure in Gegenwart von Fumarsäure zu bestimmen.

Résumé—On propose une nouvelle méthode colorimétrique pour le dosage de l'acide maléique. On a trouvé que, parmi les acides aliphatiques dicarboxyliques essayés, l'acide maléique est extrait sélectivement en nitrobenzène en tant que complexe d'association ionique rouge (λ max. 516 nm) formé entre l'anion hydrogénomaléate et le cation tris(1,10-phénanthroline)fer(II). Une quantité molaire au moins 32 fois supérieure de tris (1,10-phénanthroline)fer(II) par rapport à l'acide maléique est nécessaire, et le domaine de pH optimal est de 3–5. On obtient une relation linéaire dans le domaine de concentrations 10^{-5}–10^{-4} M en acide maléique. L'écart type relatif est de 1,0%. L'intensité de coloration de l'extrait reste constante à température ordinaire pendant au moins 24 h. Une grande quantité d'acide fumarique, l'isomère *trans* de l'acide maléique, n'est pas extraite dans les mêmes conditions. Ceci rend possible le dosage de l'acide maléique en la présence d'acide fumarique.

REFERENCES

1. A. L. Markman and E. G. Chikryzova, *Tr. Tashkentsk. Politekhn. Inst.*, 1963, **22**, 29.
2. W. Funasaka, T. Kojima and K. Fujimura, *Bunseki Kagaku*, 1964, **13**, 42.
3. K. Burger and E. Schulek, *Z. Anal. Chem.*, 1960, **172**, 98.
4. A. P. Kreshkov, L. N. Byokova and N. T. Smolova, *Zh. Analit. Khim.*, 1964, **19**, 156.
5. Y. Yamamoto, K. Kotsuji and S. Tanaka, *Bull. Chem. Soc. Japan*, 1965, **38**, 499.
6. K. Kotsuji, T. Sakurai and Y. Yamamoto, *Nippon Kagaku Zasshi*, 1965, **86**, 519.

7. S. Hayashi, K. Kotsuji, T. Sakurai, K. Kimura and Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1965, **38**, 1494.
8. Y. Yamamoto, N. Okamoto and E. Tao, *Bunseki Kagaku*, 1965, **14**, 343.
9. T. Kumamaru, Y. Hayashi, N. Okamoto, E. Tao and Y. Yamamoto, *Anal. Chim. Acta.*, 1966, **35**, 524.
10. N. E. Topp and C. W. Davies, *J. Chem. Soc.*, 1940, 87.
11. Y. Yamamoto, S. Kikuchi, Y. Hayashi and T. Kumamaru, *Bunseki Kagaku*, 1967, **16**, 931.
12. Y. Yamamoto, N. Okamoto and E. Tao, *Anal. Chim. Acta*, 1969, **47**, 127.
13. Y. Yamamoto, T. Kumamaru, A. Tatehata and N. Yamada, *ibid.*, 1970, **50**, 433.
14. Y. Yamamoto, T. Tarumoto and M. Tsubouchi, *Bull. Chem. Soc. Japan*, 1971, **44**, 2124.

Talanta, 1972, Vol. 19, pp. 423 to 437. Pergamon Press. Printed in Northern Ireland

STUDIES ON INTERFACIAL ELECTROCHEMICAL PHENOMENA IN PIGMENT-VEHICLE SYSTEMS

YOSHIAKI ŌYABU
Nippon Paint Co., Ltd., 246 Kyu-Iketanaka, oaza-Ikeda, Neyagawa,
Osaka, Japan

and

YOSHIKAZU YASUMORI
Yanagimoto Mfg. Co., Ltd., 28 Joshungamae-cho, Shimotoba, Fushimi-ku,
Kyoto, Japan

(*Received* 17 *June* 1971, *Accepted* 31 *August* 1971)

Summary—Sedimentation potentials under a centrifugal field are studied with the disperse system titanium dioxide, alkyd resin and xylene. The relationships between the sedimentation potential and the rotation speed, the distance apart of the electrodes in the cell and the total weight of particles in the disperse system are examined. From the theoretical evaluation of the initial sedimentation potential, the zeta potential of the pigment in the disperse system is calculated. The calculated value was almost coincident with that obtained by the electrophoretic method. As the sedimentation potential is proportional to the total weight of pigment in the space between the electrodes in the cell, the particle-size distribution of pigment can be obtained from the sedimentation potential-time curve. The particle-size distribution in the above-mentioned disperse system was examined with respect to the effect of rotation speed and the pigment content. The modal diameter for the particle-size distribution obtained by this method had almost the same value as that obtained by the electron microscope method. By use of this method for particle-size analysis, the particle-size distribution for particles of diameter <1 μm can be obtained in a short time (*ca.* 10–30 min) and the zeta potential of the particles in the disperse system can be calculated.

MEASUREMENT OF SEDIMENTATION POTENTIAL IN NON-AQUEOUS DISPERSE SYSTEMS AND ITS THEORETICAL EVALUATION

PREVIOUSLY, one of the authors has measured the electrophoretic velocities of particles in a non-aqueous disperse system and from those results calculated the zeta potential by using the Helmholtz equation, and pointed out that the stability of a disperse system is dependent on the charges of the particles even in a non-aqueous system of low dielectric constant.[1,2]

This paper describes the measurement of sedimentation potential of particles in a non-aqueous disperse system under a centrifugal field.[3]

EXPERIMENTAL

Instrument

The centrifuge was driven by a belt connecting it to a motor *via* a set of interchangeable pulleys giving speeds of 250, 520, 1050 and 1560 rpm. The input impedance of the amplifier for measurement of the sedimentation potential was $>10^{12}$ ohm and the total sensitivity of the amplifier and the recorder was 1 mV for full-scale deflection. The sensitivity could be reduced by means of voltage dividers applied to the input and output signals of the amplifier.

The construction of the sample cell is shown in Fig. 1. The cell is made of Teflon, and the platinum ring-shaped electrodes have an inner diameter of 8 mm. The distance between the two electrodes is variable in 5 steps: 20, 25, 30, 35 and 40 mm.

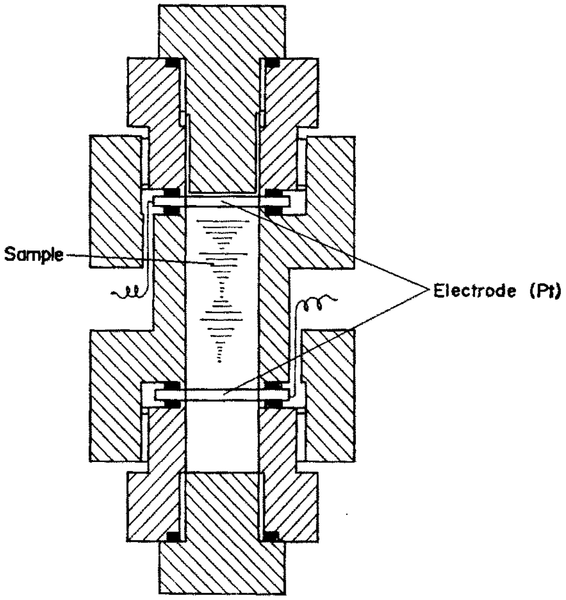


FIG. 1.—Construction of the cell.

Materials and sample preparation

An oily short-chain alkyd resin dissolved in xylene was used as the dispersion medium and titanium dioxides *A*, *B* and *C* as the dispersed phase. *A* was a non-surface-treated grade, *B* was treated with aluminium oxide, zinc oxide and silica, and *C* was for use in paint.

The disperse systems were prepared at several concentrations, after dispersing 10% pigment in 5% resin solution with a ball mill. The final disperse system was agitated for at least 30 min (usually 30–60 min) to give a reproducible dispersion of the particles in each run.

Procedure

The validity of the following equations was examined [for symbolism see below; *cf.* appendix, equations (6) and (12′)].[4]

$$(E_{\text{sed}})_{t=0} = k_2 \cdot \frac{r_1 + r_2}{2} \cdot \omega^2 \cdot \frac{3W}{4\pi\rho} \tag{1}$$

$$k_2 = \frac{(\rho - \rho_0)D_0\zeta f}{3K\eta_0} \tag{2}$$

It was assumed that each particle had the same zeta potential. Other values of the factors of the sedimentation potential were measured as follows. The viscosity of the dispersion medium was measured with an Ostwald viscometer and the electric conductivity by the current flowing on applying a d.c. voltage across the cell electrodes. The dielectric constant was measured with 1 kHz. As the dielectric constant used for calculation of the zeta potential should be that at the interface between the particle and the medium, but we assumed for convenience that the dielectric constant was almost constant in the whole liquid phase.

The distance between the rotating axis and the electrodes was designed to be large enough to be taken as practically equal for both electrodes. This is necessary for the simple treatment, because the centrifugal force acting on the particles is proportional to the distance between the rotating axis and the particle. In this instrument the distance between the furthest electrode and the rotating axis was 0·20 m. The time required to reach steady rotation was observed to be 2·5 sec at 1560 rpm, 2·0 sec at 1050 rpm, or 1·0 sec at 520 rpm.

RESULTS AND DISCUSSION

The initial sedimentation potential

An example of the sedimentation potential–time curve obtained with this instrument is shown in Fig. 2. The time required to reach the maximum potential

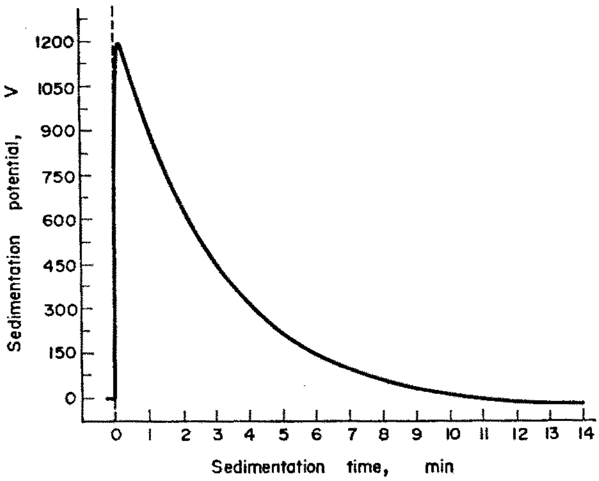


FIG. 2.—Sedimentation potential–time curve.
Suspension: TiO$_2$ *B* 5%, alkyd resin 3%, xylene 92%; 1560 rpm; 30-mm cell

was about 7 sec. Therefore the capacitance of the cell is considered to contribute to the potential decay. This consideration was supported by the fact that the time required for a steady current to flow was 7–8 sec after the voltage had been applied across the cell.

As it is very difficult to determine the amount of pigment during the sedimentation, the initial sedimentation potential should be used to calculate the zeta potential from equations (1) and (2). The authors tried to determine the initial potential by extrapolation of the curve, using two methods of filling the cell with suspension, as shown in Fig. 3. One mode is to fill with suspension just to the level of the upper

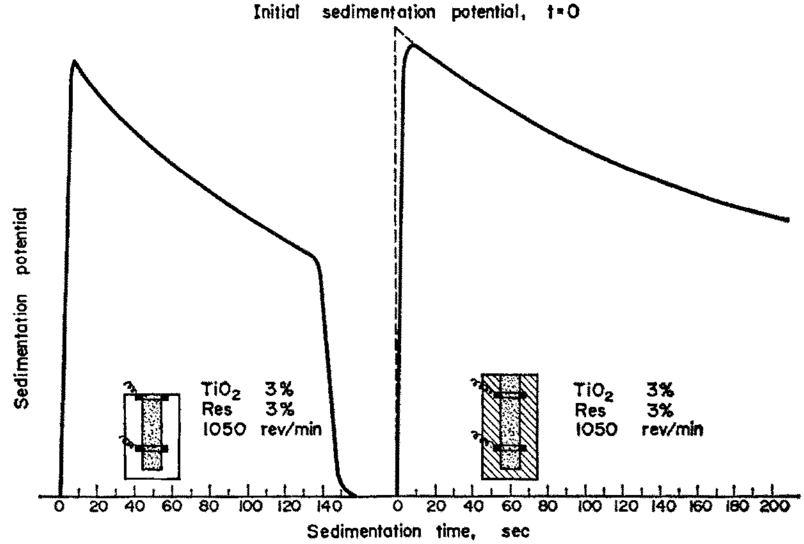


FIG. 3.—Relationship between settling rate and initial sedimentation potential, for two types of cell filling.
Sample: TiO$_2$ 3%, alkyd resin 3%; measured at 1050 rpm.

electrode (nearer to the rotating axis) as shown at the left of Fig. 3, and the other to fill it to above this level, as shown on the right. In the first mode, particles will be removed more and more from the space between the electrodes as the time elapses, and so the particle-size distribution changes immediately after the beginning of rotation. In the other, as the particles above the level of the upper electrode enter the space between the electrodes for some time after the beginning of rotation, the particle-size distribution will not change and only the distances between the particles will decrease to $1/\alpha$ of the initial distance, where $\alpha = \exp k_1\omega^2a^2t$ [*cf.* appendix equation (8)].

Therefore the sedimentation potential, E_{sed}, decreases according to the equation

$$E_{\mathrm{sed}} = \sum_{a=0}^{\infty} \frac{k_2\omega^2}{2(r_2 - r_1)} [a^3\phi(a)e^{-k_1\omega^2a^2t}({r_2}^2 - {r_1}^2e^{2k_1\omega^2a^2t})] \tag{3}$$

As $a^3\phi(a)$ for each particle size is regarded as constant for some time after the beginning of rotation, E_{sed} is expressed as the summation of linear equations of t. That is,

$$E_{\mathrm{sed}} = \sum_{a=0}^{\infty} \frac{k_2\omega^2(r_2 - r_1)}{2} a^3\phi(a)\left(1 - \frac{{r_1}^2 + {r_2}^2}{{r_2}^2 - {r_1}^2} \cdot k_1\omega^2a^2t\right) \tag{4}$$

From (4) it is obvious that the extrapolation of the sedimentation potential–time curve for the second mode of filling gives the initial sedimentation potential. This initial sedimentation potential is proportional to $(r_1 + r_2)/2$ [*cf.* appendix equation (12′)] and so we can calculate the zeta potential by equation (1). However, both extrapolation values were experimentally almost the same, when the particles were very fine and the rotation speed was small.

Relationship between the sedimentation potential and the amount of pigment particles in the space between the electrodes

Assuming that the specific gravity of the particles is independent of the diameter, the relationship between the sedimentation potential and the total weight of particles should be linear, from (4). The total weight of particles was determined by weighing the amount of solid matter obtained by drying at 105° for 3 hr a sample of suspension from the space between the electrodes, taken when the rotation was stopped. The points plotted for pigment weight *vs.* sedimentation potential lay on straight lines for various rotation speeds, the slope increasing with rotation speed, but the lines did not pass through the origin, and the value extrapolated to zero potential was 0·005 g (the initial amount of pigment was *ca.* 0·06 g). The potential decay after the centrifuge was switched off is shown at the left of Fig. 3. It took about 20 sec for rotation to cease. The error caused by sedimentation after switching off is therefore considered to be small. The inequality in centrifugal forces in the cell cannot explain the fact that the straight lines do not pass through the origin, because this effect might decrease the weight found. The discrepancy may be due to the inequality of zeta potentials for the particle systems, or to other causes. However, as the intercept was very small, the experimental results were taken as agreeing with equation (1) within experimental error.

Relationship between initial sedimentation potential and the electrode distance as well as the rotation speed

The relationship between the initial sedimentation potential and the total weight of particles at the beginning can be obtained by using cells with various electrode distances. From (1),

$$\frac{2(E_{\text{sed}})_{t=0}}{r_1 + r_2} = k_2\omega^2 W \frac{3}{4\pi\rho} \tag{5}$$

As the total weight, W, of particles in the space between the electrodes is proportional to the distance l between the two electrodes, the left-hand side (LHS) of the expression should be proportional to l and ω^2. The results obtained with various rotation speeds and distances between the electrodes gave straight-line plots which passed through the origin, showing equation (5) to be consistent with the experimental results [LHS plotted *vs.* l and $(\text{LHS})^{1/2}$ *vs.* ω].

Resistance of the cell

When the resistance of the cell containing the suspension is R,

$$R = \frac{r_2 - r_1}{\lambda} \cdot C_l \tag{6}$$

where λ is the specific conductivity of the suspension and C_l is a constant. When the electrode distance was changed, the change in R for various concentrations of particles was small. The calculated values of C_l were constant within ±3%.

Relationship between initial sedimentation potential and concentration of particles

This relationship is shown in Fig. 4. When the amount of the potential-determining alkyd resin is small compared with the amount of pigment, the special adsorption layer of alkyd resin cannot cover the particles and so the zeta potential is considered to become lower.

Relationship between zeta potential and the resin content

The zeta potential of titanium dioxide was calculated for various concentrations of alkyd resin. The results are shown in Fig. 5. Generally speaking, the lower the resin content, the higher the zeta potential. Below 0·3%, the amount of resin dissolved in the xylene becomes so small that the stability of the suspension is reduced and measurements become very difficult. These effects have been reported by van der Minne and Hermanie.[5,6]

The results shown in Fig. 5 show the same trend as those calculated[1] by the electrophoretic method. Although the former are a little lower, they are satisfactory, considering the difference in the methods.

MEASUREMENT OF PARTICLE-SIZE DISTRIBUTION IN NON-AQUEOUS DISPERSE SYSTEMS BY MEANS OF THE SEDIMENTATION POTENTIAL

In industries handling disperse systems of micro-size particles, it is very important to measure the state of dispersion. Among many methods defining this, the particle-size distribution is the most useful. Both the rheological and the optical properties

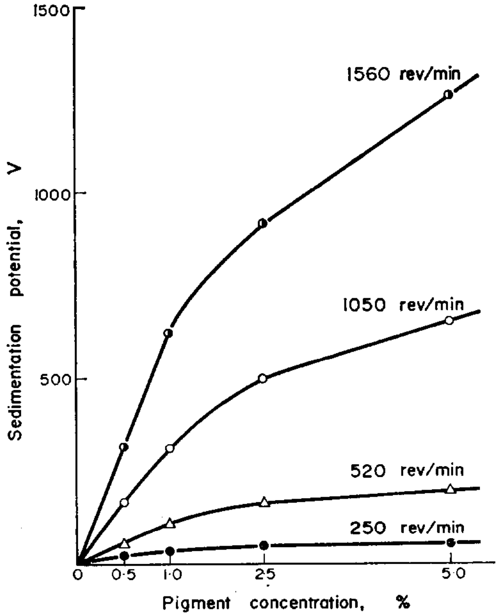


FIG. 4.—Relationship between pigment concentration and initial sedimentation potential.
Resin 3%; 30 mm-cell

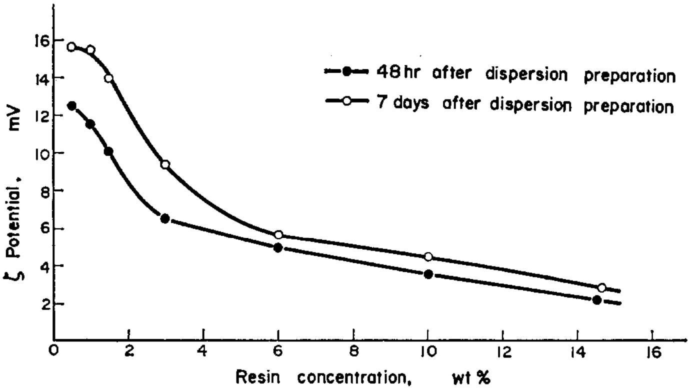


FIG. 5.—Relationship between resin concentration and zeta potential.
Pigment 1%

of the dispersed system change with the particle-size distribution. In industrial applications it is most desirable to know this distribution. Several methods for determining the particle-size distribution are known, but some problems still exist in the preparation of samples and in the measuring systems. Here we describe the method for calculating the particle-size distribution from measurements of the sedimentation potential, where the state of the sample is the same or nearly the same as in industrial use.

It was shown above that the sedimentation potential is proportional to the total weight of particles existing in the space between the electrodes in the cell. Therefore the sedimentation potential–time curve can reflect the curve for total weight of sedimented particles *vs.* time. Then the particle-size distribution obtained from the sedimentation potential–time curve is based on the weight of particles. Strictly speaking it is based on the product of zeta potential and weight of particles, but assuming the specific gravity and the zeta potential of particles in the disperse system are independent of the diameter of the particles, the statement just made will hold true.

EXPERIMENTAL

Sample and preparation

Titanium dioxide *C* was used as before.

Conditions for measurement

All measurements were made at 25°. Because in the two-liquid-layer method the sedimentation potential in the second layer should be different from the initial sedimentation potential, and so the particle-size distribution should deviate from the initial distribution, the homogeneous liquid method was used. In the homogeneous liquid method it must be noted that the dispersed state of the sample and the time required for measurement play the most important parts.

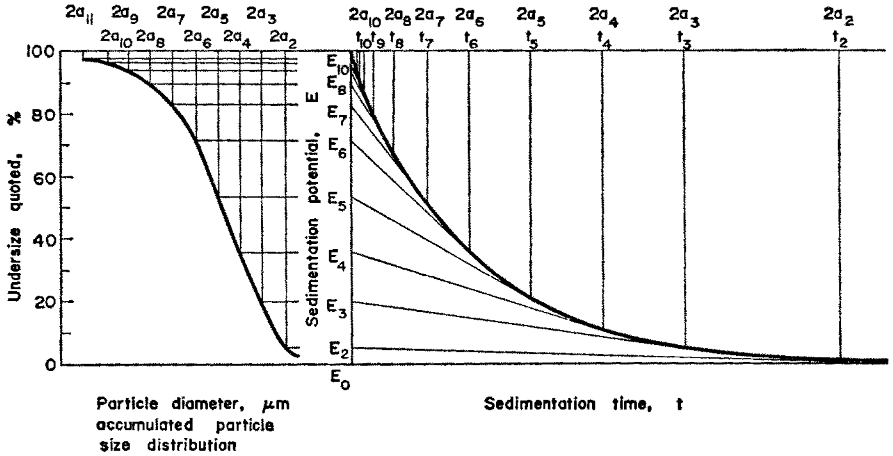


FIG. 6.—Construction of cumulative particle-size distribution diagram from sedimentation potential–time curve.

Configuration of particle-size distribution curve

When the radius of the largest particles still existing in the space between the electrodes at time t after the beginning of centrifugation is a_m, t can be calculated for each given a_m from $t = ln\,(r_2/r_1)/k_1\omega^2 a_m^2$ [cf. appendix equation (12)]. So the first step for obtaining the particle-size distribution curve is to calculate t for each increment of 0·05 μm in a_m <0·5 μm and of 0·1 μm in a_m > 0·5 μm. Then the extrapolation to $t = 0$ of the tangent to the sedimentation potential–time curve at t gives the ordinate of the cumulative particle-size distribution curve at a_m. An example is shown in Fig. 6.

RESULTS AND DISCUSSION

Theoretical calculation of the particle-size distribution from the sedimentation potential

In sedimentation under a centrifugal field, the centrifugal force on a particle is proportional to the distance between the particle and the rotating axis. Therefore the force is a function of sedimentation time. On this basis equation (7) can be derived relating the particle-size distribution to the sedimentation potential [*cf.* appendix equation (12)].

$$E_{\text{sed}} = \frac{k_2\omega^2}{2(r_2 - r_1)} \times \int_0^{a_t} a^3\phi(a)(r_2{}^2e^{-k_1\omega^2a^2t} - r_1{}^2e^{k_1\omega^2a^2t})\,da \qquad (7)$$

where $a_t = (\ln (r_2/r_1)/k_1\omega^2t_2)^{1/2}$, and k_1 is a constant related to the viscosity and density of the dispersion medium or the suspension; k_2 is a constant related to the viscosity, density, dielectric constant and electric conductivity of the dispersion medium and zeta potential of the particles in suspension; r_1 and r_2 are the radii of rotation of the electrodes. On putting $t = 0$ we obtain

$$(E_{\text{sed}})_{t=0} = k_2\omega^2 \frac{r_1 + r_2}{2} \int_0^{\infty} a^3\phi(a)\,da \qquad (8)$$

Therefore the initial sedimentation potential is equal to the potential which all particles would exhibit if they were gathered at the middle plane between the two electrodes.

Dependence of the particle-size distribution on the conditions of measurement

Typical sedimentation potential–time curves for titanium dioxide *C* in various concentrations are shown in Fig. 7 and the particle-size distribution curves derived are shown in Fig. 8. Table 1 gives the model and median diameters for each rotation speed and pigment content.

Effect of the pigment content. The pigment content has no large effect on the cumulative particle-size distribution curve, but there is a tendency for the number

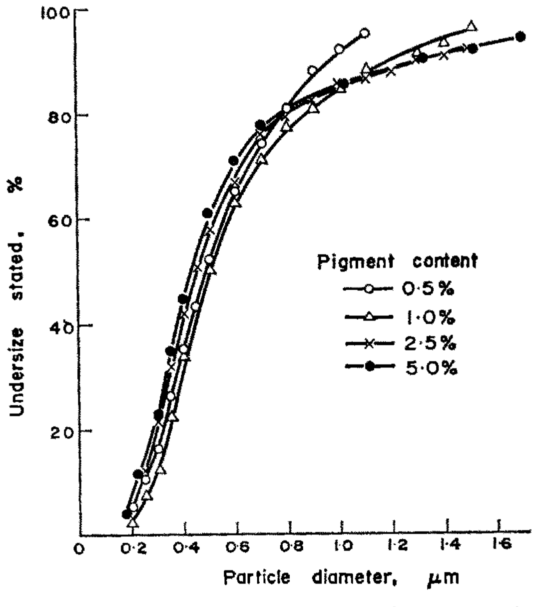


FIG. 7.—Cumulative particle-size distribution measured at 520 rpm.

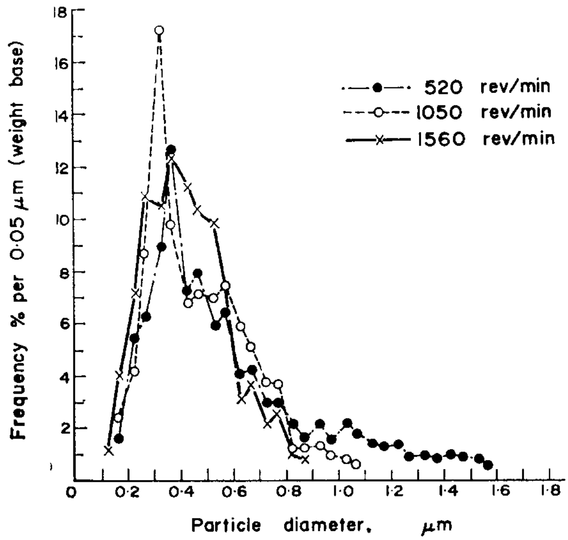


FIG. 8.—Particle-size distribution measured on a 1% suspension of pigment.

of large particles to increase as the pigment concentration increases. This may be caused by an increase in the number flocculated particles, but both the model and median diameters coincide within 0·1 μm, though the latter are inclined to decrease with increase in pigment concentration.

TABLE I.—RELATIONSHIPS OF THE MODAL AND MEDIAN DIAMETERS TO THE ROTATION SPEED AND PIGMENT CONTENT

Pigment concentration %		Diameter, μm 520 rpm	1050 rpm	1560 rpm
0·5	Mode	0·30–0·35	0·35–0·40	0·35–0·40
	Median	0·48	0·48	0·38
1·0	Mode	0·35–0·40	0·30–0·35	0·35–0·40
	Median	0·49	0·45	0·42
2·5	Mode	0·30–0·35	0·35–0·40	0·35–0·40
	Median	0·44	0·43	0·39
5·0	Mode	0·30–0·35	0·30–0·35	0·35–0·40
	Median	0·42	0·42	0·38

Effect of the rotation speed. The rotation speed is recognized as having little effect on the distribution curve. In the figures the distribution was plotted for 0·05 μm intervals. If the distribution at 0·1 μm intervals had been plotted, the curves would have agreed better. The differences for the larger particles are perhaps due to errors in drawing.

Comparison between the distribution curves obtained by the sedimentation potential and the electron microscope methods. In Fig. 9 are shown the distribution curves based on particle weight and on number of particles. Figure 10 shows the distribution

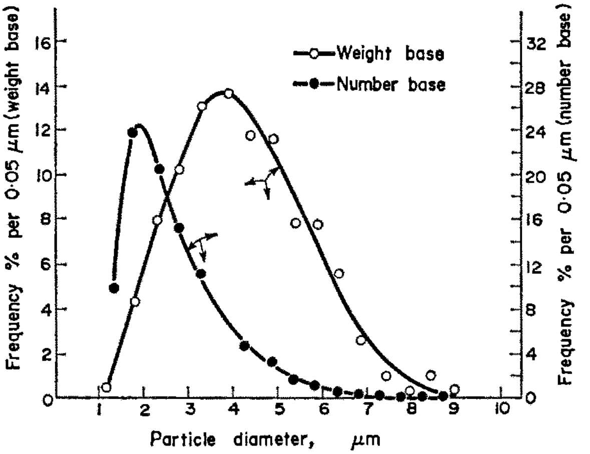


FIG. 9.—Relationship between particle-size distributions on weight base and number base.
Measured at 1560 rpm, 0.5% pigment, sedimentation potential method

curve obtained by the measurement of the fixed-direction diameter for 1000 particles by electron microscope.

The distribution-curve obtained by the electron microscope method is based on number of particles and that from the sedimentation potential method is based on particle weight (strictly, on the product of the weight and zeta potential of the particle). For comparison, weight-base and number-base distribution curves are both plotted in Figs. 9 and 10.

In the electron microscope method, combined images of particles are not counted, as the images of aggregated particles cannot be distinguished from overlapping images of separate particles. Because aggregated particles are not counted, the

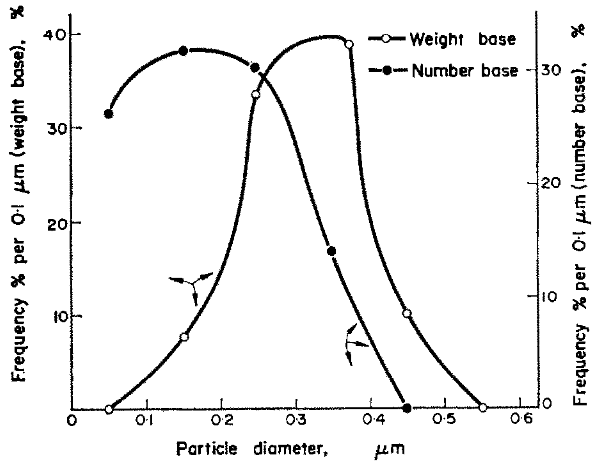


FIG. 10.—Relationship between particle-size distribution on weight and number base.
Electron microscope method.

single particle concentration becomes higher. For this reason the particle-size distribution curve deviates noticeably from a logarithmic normal distribution curve. On the other hand, in the sedimentation potential method the particle size means the diameter of particle which moves as a kinetic unit in the disperse system. Therefore the distribution curve is similar to the logarithmic normal distribution curve, because the aggregated particles are counted. The model diameters (two methods of measurement) were 0·3–0·4 μm based on the particle weight and about 0·2 μm based on the number of particles.

SYMBOLS

E_{sed}	sedimentation potential
I_{str}	streaming current
Q	total charge of the particle
z	charge per unit area around the particle
θ	potential around the particle
A	cross-sectional area of the cell
r_1	rotation radius of the electrode nearest to the rotating axis
r_2	rotation radius of the electrode furthest from the rotating axis
ω	rotation speed
W	total weight of the particles existing in the space between the two electrodes in the cell
ρ	density of the particle
ρ_0	density of dispersion medium
K	specific electric conductivity of the dispersion medium
D_0	dielectric constant of the dispersion medium
η_0	viscosity of the dispersion medium
ζ	zeta potential of the particle in the dispersion medium
a	radius of the particle
V	gradient of the sedimentation potential
g	acceleration of the kinetic field
f	retardation coefficient
n_0	number of particles in unit volume
n	total number of particles existing in the space between the two electrodes in the cell
χ	reciprocal of the thickness of the electrical double layer
$\phi(a)$	distribution of the particle of radius a
k_1	velocity constant of sedimentation
k_2	potential constant of sedimentation

Zusammenfassung—Sedimentationspotentiale in einem Zentrifugalfeld wurden an der Dispersion aus Titandioxid, Alkydharz und Xylol studiert. Die Beziehungen zwischen Sedimentationspotential und Rotationsgeschwindigkeit, Abstand von den Elektroden in der Zelle und Gesamtgewicht der Teilchen in der Dispersion werden untersucht. Aus der theoretischen Berechnung des anfänglichen Sedimentationspotentials wird das Zeta-Potential des Pigments in der Dispersion berechnet. Der berechnete Wert fiel mit dem elektrophoretisch ermittelten fast zusammen. Da das Sedimentationspotential proportional ist zum Gesamtgewicht des Pigments im Raum zwischen den Elektroden in der Zelle, kann man aus der Kurve, die das Sedimentationspotential in Abhängigkeit von der Zeit wiedergibt, die Teilchengrößenverteilung des Pigments erhalten. Die Teilchengrößenverteilung in der erwähnten Dispersion wurde im Hinblick auf den Einfluß von Rotationsgeschwindigkeit und Pigmentanteil untersucht. Der äquivalente Durchmesser der Teilchengrößenverteilung, der auf diese Weise erhalten wurde, war fast gleich dem elektronenmikroskopisch ermittelten. Verwendet man dieses Verfahren für die Teilchengrößenanalyse, so kann man die Größenverteilung bei Teilchen mit Durchmessern <1 μm in kurzer Zeit (*ca.* 10–30 min) erhalten und das Zeta-Potential der Teilchen in der Dispersion berechnen.

Résumé—On étudie les potentiels de sédimentation dans un champ centrifuge avec le système dispersé dioxyde de titane, résine alkyde et xylène. On examine les relations entre le potentiel de sédimentation et la vitesse de rotation, l'éloignement des électrodes dans la cellule et le poids total des particules dans le système dispersé. De l'évaluation théorique du potentiel de sédimentation initial, on calcule le potentiel dzéta du pigment dans le système dispersé. La valeur calculée coïncide presque avec celle obtenue par la méthode électrophorétique. Comme le potentiel de sédimentation est proportionnel au poids total de pigment dans l'espace entre les électrodes dans la cellule, la répartition du pigment par dimensions de particules peut être obtenue à partir de la courbe potentiel de sédimentation—temps. La répartition par dimensionsde particules dans le système dispersé mentionné ci-dessus a été examinée par rapport à l'influence de la vitesse de rotation et de la teneur en pigment. Le diamètre modal pour la répartition par dimensions de particules obtenu par cette méthode a presque la même valeur que celle obtenue par la méthode au microscope électronique. En utilisant cette méthode pour l'analyse de dimensions de particules, on peut obtenir la répartition par dimensions de particules en un temps court (environ 10–30 mn) pour des particules de diamètre <1 μm, et l'on peut calculer le potentiel dzéta des particules dans le système dispersé.

REFERENCES

1. Y. Oyabu, H. Kawai and Y. Nakanishi, *Color Material*, 1962, **35**, 98.
2. *Idem*, *ibid.*, 1964, **37**, 138.
3. Y. Oyabu, *ibid.*, 1970, **43**, 108.
4. J. T. Davies and E. K. Rideal, '*Interfacial Phenomena*', p. 138. Academic Press, New York, 1963.
5. J. L. Van der Minne and P. H. J. Hermanie, *J. Colloid Sci.*, 1952, **7**, 600.
6. *Idem*, *ibid.*, 1953, **8**, 38.

APPENDIX

The sedimentation potential and the particle-size distribution

The following five assumptions were made for the theoretical derivation of the sedimentation potential under the centrifugal field as a function of the particle-size distribution.

(1) The particle is a sphere and is not combined.
(2) The particle is very small and settles out in a laminar flow.
(3) The retardation of the sedimentation velocity induced by the particle charge can be neglected.
(4) All particles have equal density and equal zeta potential.
(5) The electrical conductivity of the suspension is not affected by the pigment content.

When the particles settle out from the dispersion medium, the kinetic equation for the stationary velocity of particles is

$$\frac{4}{3}\pi(\rho - \rho_0)a^3\omega^2x = 6\pi\eta_0 a\frac{\mathrm{d}x}{\mathrm{d}t} \tag{1}$$

where x is the distance between the rotating axis and a particle at time t. From (1),

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{2}{9}\cdot\frac{\rho - \rho_0}{\eta_0}\omega^2a^2x \tag{2}$$

$$= k_1\omega^2a^2x \tag{2'}$$

where

$$k_1 = \frac{2(\rho - \rho_0)}{9\eta_0} \tag{3}$$

Solving the differential equation (2′),

$$\ln x = k\omega^2a^2t + \text{constant}$$

If the distance of the particle from the axis is r_1 when $t = 0$,

$$\text{constant} = \ln r_1$$

and

$$\ln\frac{x}{r_i} = k_1\omega^2a^2t \tag{4}$$

$$x = r_ie^{k_1\omega^2a^2t} \tag{4'}$$

On the other hand, when the homogeneously dispersed spherical particles settle out, the gradient of sedimentation potential is,[4]

$$V = \frac{a^3(\rho - \rho_0)n_0gD_0\theta}{3K\eta_0}$$

When the ratio of the radius of the particle to the thickness of the electrical double layer, χa, is negligible compared to unity, this equation should be written as

$$V = \frac{a^3(\rho - \rho_0)n_0gD_0\theta f}{3K\eta_0}$$

where if the particle is a sphere, f is equal to 2/3.

The sedimentation potential, E_{sed}, *i.e.*, the difference between the potentials of the two electrodes is

$$E_{\text{sed}} = V(r_2 - r_1)$$

$$= \frac{a^3(\rho - \rho_0)n_0(r_2 - r_1)gD_0\theta f}{3K\eta_0}$$

When the cross-sectional area of the cell is A, the total number of particles in the space between the two electrodes, n, is $An_0(r_2 - r_1)$. When n is used instead of n_0 in the equation above, KA should be used instead of K.

Therefore

$$E_{\text{sed}} = \frac{a^3(\rho - \rho_0)ngD_0\theta f}{3K\eta_0}$$

When the number of particles existing in the space between x and $x + \mathrm{d}x$ away from the rotating axis is Δn, the sedimentation potential ΔE_{sed} across this space is given by

$$\Delta E_{\text{sed}} = \frac{a^3(\rho - \rho_0)\Delta n \cdot \omega^2xD_0\theta f}{3K\eta_0} \tag{5}$$

$$= k_2a^3\Delta n \cdot \omega^2x \cdot f \tag{5'}$$

where

$$g = \omega^2x$$

$$k_2 = \frac{(\rho - \rho_0)D_0\theta f}{3K\eta_0} \tag{6}$$

The total weight of particles W in the space between the electrodes is

$$W = \frac{4}{3}\pi\rho\int_0^\infty a^3\phi(a)\,\mathrm{d}a \tag{7}$$

From (4′), writing x_t for the distance (at time t) between the axis and the particle which was initially at a distance x from the axis,

$$x_t = xe^{k_1\omega^2a^2t}$$

and putting $x_t + \alpha\Delta x$ for the distance (at time t) between the axis and the particle which was initially $x + \Delta x$ from the axis,

$$x_t + \alpha\Delta x = (x + \Delta x)e^{k_1\omega^2a^2t}$$

Therefore

$$\alpha = e^{k_1\omega^2a^2t} \tag{8}$$

This equation shows that the rate of change of the number of particles in a differential space during centrifuging is $1/\alpha$ and independent of the initial distance x. Hence the number of particles existing in a thickness $\mathrm{d}x$ of suspension at t can be expressed by

$$\phi(a)\cdot\frac{\mathrm{d}x}{\alpha(r_2 - r_1)} = \frac{\phi(a)\,\mathrm{d}x}{(r_2 - r_1)e^{k_1\omega^2a^2t}}$$

Then the sedimentation potential of a particle of radius a at time t can be written as follows from (5′):

$$(E_{\mathrm{sed}})_{a.} = \int_{x_1}^{x_2} k_2 a^3 \omega^2 x \cdot \frac{\phi(a)}{(r_2 - r_1) e^{k_1 \omega^2 a^3 t}} \cdot \mathrm{d}x$$

$$= \frac{k_2 \omega^2}{2(r_2 - r_1)} \left[\frac{a^3 \phi(a)}{e^{k_1 \omega^2 a^2 t}} (r_2^2 - x_1^2) \right] \tag{9}$$

where x_1 is the distance between the rotating axis and the particle initially nearest to it at t. So from (4′)

$$x_1 = r, e^{k_1 \omega^2 a^2 t}$$

Substituting this expression for x_1 into (9) we have,

$$(E_{\mathrm{sed}})_{a,t} = \frac{k_2 \omega^2}{2(r_2 - r_1)} \left[\frac{a^3 \phi(a) (r_2^2 - r, e^{2k_1 \omega^2 a^2 t})}{e^{k_1 \omega^2 a^2 t}} \right] \tag{10}$$

The largest particles among those existing in the space between the electrodes at t reach a distance r_2 from the axis, if they were at distance r_1 initially. Putting the largest radius as a_{m}, from (4′), we have

$$r_2 = r_1, e^{k_1 a_m^2 \omega^2 t}$$

$$A_{\mathrm{m}} = \sqrt{\frac{\ln (r_2/r_1)}{k_1 \omega^2 t}} \tag{11}$$

Therefore the sedimentation potential for all particles at t is obtained by integrating (10) with respect to the radii of the particles.

$$(E_{\mathrm{sed}})_t = \frac{k_2 a^2}{2(r_2 - r_1} \int_0^{a_m} \frac{a^3 \phi(a)(r_2^2 - v_1^2 e^{2k_1 \omega^2 a^2 t}}{e^{k_1 \omega^2 a^2 t}} \, \mathrm{d}a$$

$$= \frac{k \omega^2}{2(r_2 - r_1)} \int_0^{a_m} a^3 \phi(a)(r_2^2 e^{-k_1 \omega^2 a^2 t} - r_1^2 e^{k_1 \omega^2 a^2 t}) \, \mathrm{d}a \tag{12}$$

And when $t = 0$, a_{m} is infinity from (11), and so (12) is written as follows, from (7).

$$(E_{\mathrm{sed}})_{t=0} = \frac{k_2 \omega^2}{2(r_2 - r_1)} \cdot (r_2^2 - r_1^2) \int_0^{\infty} a^3 \phi(a) \, \mathrm{d}a$$

$$= k_2 \cdot \frac{r_1 + r_2}{2} \cdot \omega^2 \cdot \frac{3\overline{W}}{4\pi\rho} \tag{12′}$$

This equation shows that the sedimentation potential at $t = 0$ is equal to the sedimentation potential which would be generated if all the particles were at the middle plane between the two electrodes.

Derivation of the equation for the sedimentation potential

The curve for the potential distribution round a particle in the dispersion medium is very complex, even if the particle is spherical, but it can be expressed approximately as follows:

$$\theta = \theta_0 \frac{a}{y} e^{-\chi(y-a)} \tag{13}$$

where θ is the potential in the medium at a distance y from the centre of the particle and θ_0 is the potential of the particle. On the other hand, the charge per unit area around the particle is as follows, by the Poisson equation:

$$z = -\frac{D_0}{4\pi} \frac{\partial^2 \phi}{\partial y^2} \tag{14}$$

Since $\partial\theta/\partial y = 0$ inside the particle, the charge at the interface of the particle and medium, z_0, is expressed by

$$z_0 = -\frac{D_0}{4\pi} \left(\frac{\partial \theta}{\partial y} \right)_{y=a} \tag{15}$$

By substituting (13),

$$\frac{\partial\theta}{\partial y} = \frac{\theta_0 a}{y}(1 + \chi y)e^{-\chi(y-a)} \tag{16}$$

From (15) and (16)

$$z_0 = \frac{D_0\theta_0}{4\pi a}(1 + \chi a)$$

Therefore the total charge, Q, of the particle is

$$Q = \theta_0 D_0 a(1 + \chi a) \tag{17}$$

When the dispersion medium is a non-aqueous solution, the zeta potential is nearly equal to the surface potential. Then substituting ζ for θ_0 in (17), we have

$$Q = \zeta D_0 a(1 + \chi a) \tag{17'}$$

Assuming χa is negligible compared to unity, for non-aqueous medium,

$$Q = \zeta D_0 a \tag{18}$$

and the number of particles passing across the cross-section of the cell in unit time is $An_0(dx/dt)$. Then from (18) and (2) the streaming current, I_{str}, is given by

$$I_{str} = \frac{2An_0(\rho - \rho_0)a^3\omega^2 x\zeta D}{9\eta_0} \tag{19}$$

This streaming current is responsible for the streaming potential, E_{str}. At steady state it must be balanced by a current which accords with Ohm's law. This back-current is expressed by

$$I' = -\frac{AKE_{str}}{l} \tag{20}$$

where l is the distance between the two electrodes with which the potential is measured.

When the input impedance of the amplifier for the measurement of potential large enough for the current flowing out of the cell, to be neglected,

$$I_{str} + I' = 0 \tag{21}$$

Substituting (19) and (20) into (21),

$$E_{sed} = \frac{2n_0 a^3 l(\rho - \rho_0)\omega^2 x\zeta D_0}{9K\eta_0}$$

Putting $n = n_0 l$

$$E_{sed} = \frac{2a^3 n(\rho - \rho_0)\omega^2 x\zeta D_0}{9K\eta_0} \tag{22}$$

For a spherical particle, the retardation coefficient (or shape factor) f is 2/3. Hence

$$E_{sed} = \frac{a^3 n(\rho - \rho_0)\omega^2 x\zeta D_0}{3K\eta_0} \tag{23}$$

Talanta, 1972, Vol. 19, pp. 439 to 450. Pergamon Press. Printed in Northern Ireland

MECHANISM AND ANALYTICAL ASPECTS OF THE POLAROGRAPHIC MAXIMUM WAVE OF TELLURIUM

MUTSUAKI SHINAGAWA, NOBUYUKI YANO and TAKEYUKI KUROSU
Department of Nuclear Engineering, Faculty of Engineering, Osaka University,
Yamadakami, Suita-shi, Osaka, Japan

(*Received* 19 *June* 1971. *Accepted* 24 *November* 1971)

Summary—The polarogram of tellurium(IV) in weakly basic solution has a sharp maximum on the diffusion current plateau. The electrode process causing this maximum has been examined by means of various techniques such as semiconductor catalysis, "block" polarography and ultraviolet irradiation of the dropping mercury electrode. The maximum was found to be caused by the catalytic wave of hydrogen produced by the tellurium deposited on the mercury surface. Part of the tellurium is reduced to hydrogen telluride by nascent hydrogen formed catalytically. The brown mist which usually appears in the vicinity of the surface of the dropping mercury cathode consists of elemental tellurium produced by the decomposition of the hydrogen telluride near the electrode. The sudden decrease in the current maximum at a potential more negative than the peak potential of the maximum is due to desorption of tellurium, caused by movement of mercury.

THE POLAROGRAPHIC MAXIMUM of tellurium was found in 1935 by Schwaer and Suchy,[1] who said that this maximum seemed to be closely connected with the reduction of the hydrogen ion. Lingane and Niedrach[2,3] reported that this maximum was probably due to catalytic reduction of the hydrogen ion in acidic solution, and they found that a brown mist formed in the vicinity of the dropping mercury electrode (d.m.e.). Von Stackelberg *et al.*[4,5] reported on the mechanism of the generation of brown mist and the polarographic maximum. Since then, several papers[6–8] concerning the polarographic reduction of Te(IV) have appeared.

The polarographic reduction of Te(VI) was described by Norton *et al.*[9] in 1953, and again a maximum appeared which depended on the nature of the sample solution. Further reports[5,10,11] on the polarographic reduction of Te(VI) discuss the nature of the maximum.

In earlier papers,[12,13] we reported obtaining a maximum wave of similar kind when polarographing a suspension of tellurium powder in ammonium chloride solution. When a piece of tellurium block was put into contact with the d.m.e., the same kind of maximum wave was observed. Irradiation of the d.m.e. with ultraviolet light depressed the maximum current, and when the irradiation was stopped the current recovered. On the basis of these results, the mechanism of the tellurium maximum has to be reconsidered.

EXPERIMENTAL

Tellurium ingot (99·9999% purity; Osaka Asahi Metal Mfg. Co. Ltd.) was cut into pieces or ground into powder in an agate mortar.

Tellurium in the form of TeO_2, TeO_3, H_2TeO_3, K_2TeO_3, $(NH_4)_2TeO_3$, H_6TeO_6 and $NH_4HTeO_4{\cdot}2H_2O$ was obtained in chemically pure grade.

A Yanagimoto P-8 type polarograph was used for the d.m.e. work, and a Yanagimoto VE-3 type automatic apparatus for constant-potential electrolysis was used for the work with a mercury pool cathode and a carbon rod anode.

In the "suspension polarography" the sample solution was prepared by adding powdered metallic tellurium or a tellurium compound to the electrolyte solution, and current–potential curves were recorded with use of the d.m.e. while the sample solution was stirred magnetically. Rate of stirring, temperature of the solution (25° ± 0·1°) and other experimental conditions were kept constant. The conditions for the d.m.e. were: $t = 6{\cdot}0$ sec (open circuit in $1M$ ammonium chloride), $m = 0{\cdot}60$ mg/sec, and $h = 45$ cm. All batches of the electrolytic solution were deaerated with nitrogen before the electrolyses.

A piece of tellurium block was pasted on an end of a glass rod. The block was kept in contact with the hanging mercury drop (see Fig. 3A), and the current–potential curves were recorded by polarograph. This will be called the "block polarograph."

Instantaneous current–time curves were recorded oscillographically with an Iwasaki Synchroscope Model SS-5302 with SP-20 DF-A preamplifier and the Shimadzu Electropotentiostat Model SP-1.

An Ushio Uniarc-250 UR-3 apparatus was used to irradiate the d.m.e. The sample solution was deaerated with nitrogen before use. Experiments were carried out in the dark.

The hydrogen content of the evolved gas was measured with a Yanagimoto Gas-Chromatograph, Model GCG-3.

RESULTS AND DISCUSSION

General characteristics of polarographic maximum of tellurium

Figure 1[(*a*)–(*c*)] shows the polarograms of Te(IV) and Te(VI) in $1M$ ammonium chloride. In the polarogram of Te(IV), the potential range A involves the reduction current due to Te(IV) → Te^0 and the ranges B, C, D, and E have been thought[14] to involve the reduction current due to Te(IV) → Te^{2-}, where B and C involve also the catalytic current.[3,5]

If the concentration of K_2TeO_3 is increased up to $3 \times 10^{-4}M$ in $1M$ ammonium chloride, i_d increases linearly, while i_{max} attains a saturation value, comforming to the Langmuir adsorption isotherm, but shows a kink of the curve at the concentration at which the brown mist appears around the d.m.e. The values of E_{decomp} and E_{max} become a little more negative with increase in Te(IV) concentration, settling at almost $-1{\cdot}15$ and $-1{\cdot}3$ V respectively (all potentials are quoted *vs.* S.C.E.). The values of $(E_{1/2})_p$ and $E_{1/2}$ are $-0{\cdot}32$ and $-0{\cdot}55$ V respectively and independent of the concentration.

With a concentration of ammonium chloride between 0·2 and $1{\cdot}2M$, there is no change in $(E_{1/2})_p$, $E_{1/2}$, E_{decomp}, E_{max}, and i_d, but i_{max} shows a two-step saturation curve, *e.g.*, plateaux at 40 μA for 0·3–$0{\cdot}7M$ NH_4Cl and at 60 μA at $>1M$ NH_4Cl, for $5 \times 10^{-4}M$ K_2TeO_3.

According to Zhdanov and Pats[7] or Lingane and Niedrach,[2] a decrease in pH makes the height of the Te(IV) maximum higher. On the other hand, in strong alkaline solution there is no maximum.[3,8]

"Suspension polarography" of tellurium powder

Figure 1[(*d*) and (*e*)] shows the polarograms for $1M$ ammonium chloride with tellurium powder (150–200 mesh). Curve (*d*) shows what happens during magnetic stirring, and (*e*) what happens after the stirring stops. Curve (*f*) shows the decay curve of i_{max} with time after the stirring stops. These techniques may be called "suspension polarography."

In the case of the suspension polarogram of tellurium powder, the reduction step Te(IV) → Te^0 as in Fig. 1(*a*) cannot be obtained, but a similar maximum is seen on curves (*d*) and (*e*). It indicates that the existence of Te(IV) in the solution is not the necessary condition for the maximum. Combining this with the further experimental

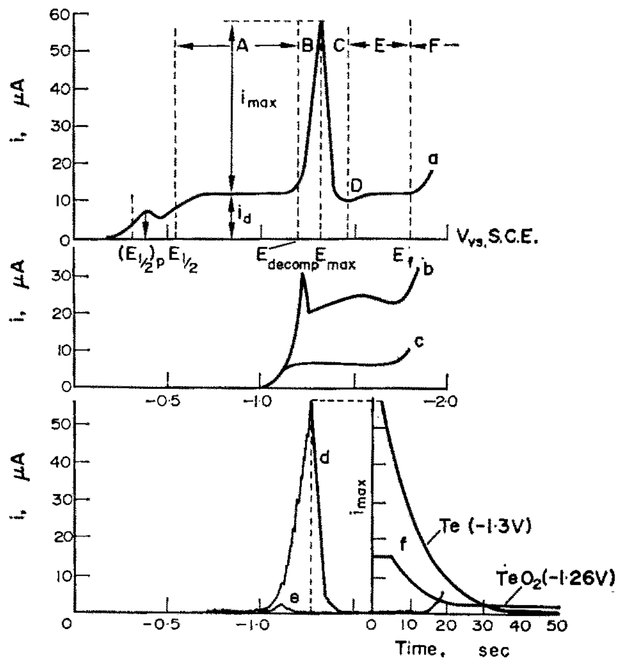


FIG. 1.—Polarograms of tellurium.
a: 1·0 × $10^{-3}M$ Te(IV) in 1*M* NH_4Cl
b: 1·0 × $10^{-3}M$ Te(VI) in 1*M* NH_4Cl
c: 0·3 × $10^{-3}M$ Te(VI) in 1*M* NH_4Cl
d: suspension polarogram while stirring; metallic Te-powder (100–150 mesh, 306 mg) in 50 ml of 1*M* NH_4Cl
e: same as *d*, but after stopping stirring
i_d: diffusion current of Te(IV) → Te^0 process
i_{max}: peak current of the maximum wave
$(E_{1/2})_p$: half-wave potential of the prewave
$E_{1/2}$: half-wave potential of the Te(IV) → Te^0 process
E_{max}: peak potential of the maximum wave
E_{decomp}: decomposition potential of the maximum wave
E_f: initial potential of the final ascent

facts to be mentioned later, it is thought that the contact of tellurium with the surface of the mercury electrode is the decisive factor in production of the maximum. So, it is considered that in ordinary polarography the elemental tellurium, reduced from Te(IV), deposits on the mercury drop and plays a role in causing the maximum.

Figure 2 shows the effects of Triton-X-100 and gelatin on the height of the maxima in suspension polarography of tellurium powder with stirring. The effects of those maximum suppressors[3,5,8] on the ordinary maximum of tellurium are illustrated for contrast, showing the same nature of the maximum, whatever its origin. The results of the current–time curves of Kuta's parabola[15] at several applied potentials are shown in Table I.

Besides elemental tellurium, TeO_2, H_2TeO_3 and $(NH_4)_2TeO_3$ powders give analogous typical maxima, but TeO_3, H_6TeO_6 or $NH_4HTeO_4{\cdot}2H_2O$ give a small maximum or none. With potassium or sodium chloride solution as supporting electrolyte a very

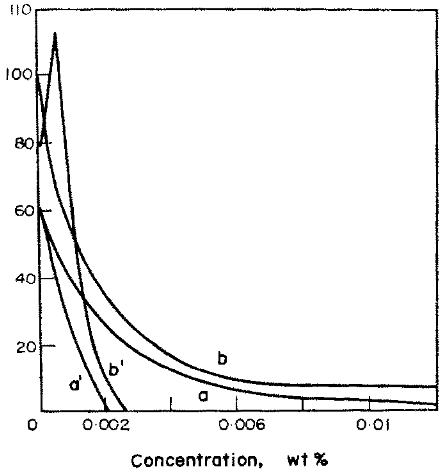


FIG. 2.—Effects of concentration of Triton-X-100 (*a*) and gelatin (*b*) on the height of the maximum in the "suspension polarogram" of 306 mg of tellurium powder in 50 ml of 1*M* NH_4Cl, and on the corresponding polarogram of 0·4 m*M* K_2TeO_3, (*a'*), (*b'*).

TABLE I.—INSTANTANEOUS CURRENT–TIME CURVES OF 1*M* NH_4Cl (50 ml) WITH SUSPENDED TELLURIUM POWDER (300 mg) AT VARIOUS CATHODE POTENTIALS

Applied voltage, *V*	−0·8	−0·9	−1·0	−1·2 (E_{decomp})	−1·3	−1·35 (E_{max})	−1·6
x of t^x	$\frac{1}{6}$	$\frac{1}{6}$	$<\frac{2}{6}$	$\frac{2·5}{6}$	$>\frac{4}{6}$	$\gg\frac{4}{6}$	$\frac{1}{6}$

$\frac{1}{6}$: diffusion current, $\frac{2}{6}$: maximum of first kind, $\frac{4}{6}$: kinetic current.

large maximum appears, but with potassium[8] or sodium[3] hydroxide the maximum is very small or non-existent.

Block polarography of elemental tellurium

A piece of elemental tellurium is placed in contact with the d.m.e. as shown in Fig. 3. The current begins at the same E_{decomp} as in suspension polarography, but increases linearly with potential sweep in accordance with Ohm's law until the block is detached from the electrode (see Fig. 3-B). It can be seen that the brown mist is spreading out and gas evolving from the whole surface of the tellurium block.

The same kind of phenomenon is seen in suspension polarography with a large particle of tellurium which might hit the mercury electrode by inertia and let the current flow even at potentials from −1·4 to −1·8 V, as shown in Fig. 4.

Adsorption of elemental tellurium on the cathode

In constant-potential electrolysis of Te(IV) in 1*M* ammonium chloride, black deposit of elemental tellurium is seen on the surface of the mercury pool cathode at more negative potentials than —0·5 V. Tellurium deposited on the mercury cathode deforms the electrocapillary curve for suspended tellurium powder (Fig. 5). The

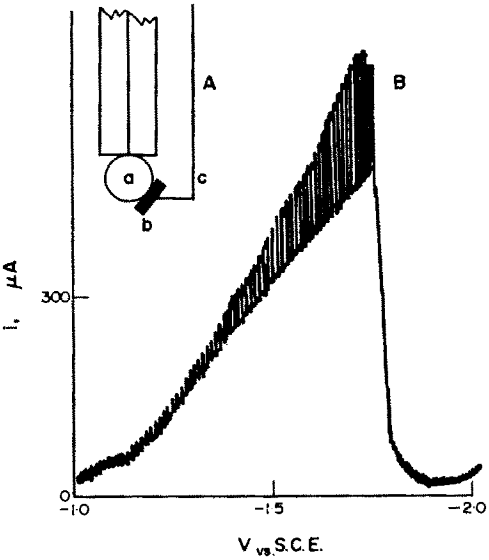


FIG. 3.—*A*: The dropping mercury cathode, in contact with a piece of elemental tellurium block pasted to the end of a glass rod. *a*: mercury drop; *b*: tellurium block; *c*: glass rod. *B*: "Block polarogram" of tellurium in 1*M* NH_4Cl.

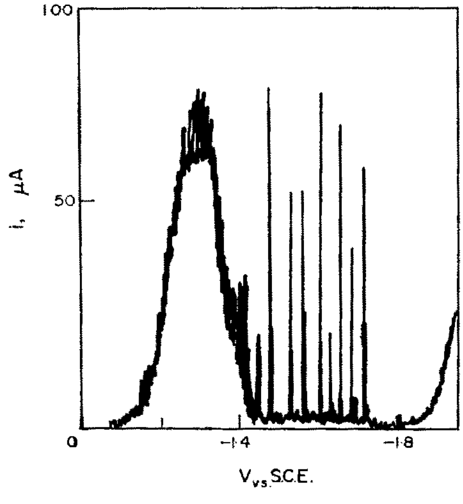


FIG. 4.—"Suspension polarograms" with tellurium powder in 1*M* NH_4Cl.
100–150 mesh

depression of the electrocapillary curve is observed just in the potential range between the beginning of the reduction wave of Te(IV) and the maximum. A small peak, *C* in Fig. 5, appears in the depression of the electrocapillary curve at the same time as sudden evolution of hydrogen from the cathode, and it is thought that desorption of elementary tellurium from the electrode makes the electrocapillary process recover synchronously. However, in the presence of gelatin in the solution the catalytic evolution of hydrogen disappears and a depression, without the small peak, is obtained. The shape of this electrocapillary curve is very similar to that of a solution composed of Te(IV), 0·3*M* ammonia and 0·1*M* ammonium chloride, given by von Stackelberg *et al.*[4,5] According to their report,[5] the presence of gelatin does not prevent the adsorption of tellurium which is electrolytically deposited, but does so with telluride.

On the other hand, according to studies at the stationary mercury electrode by Jamieson and Perone,[8] during the reduction Te(IV) → Te^0 at the d.m.e., elemental tellurium remains adhered to the electrode and this desorbs from the electrode at potentials more negative than the maximum.

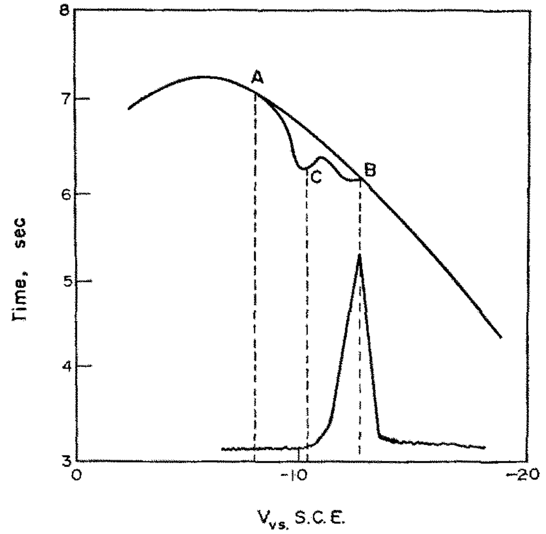


FIG. 5.—Electrocapillary curve for 1*M* NH_4Cl solution with suspended tellurium powder, compared with a "suspension polarogram" of the same solution.

By the adsorption of elemental tellurium on the mercury cathode, a "tellurium electrode" is established over the potential range between the reduction wave of Te(IV) and the maximum of the polarogram, that is the potential range *A* in Fig. 1. At a potential more negative than the maximum, already deposited tellurium departs from the mercury drop as Jamieson and Perone[8] observed for the stationary mercury electrode. This is caused by the relaxation of surface tension of mercury due to the mutual repulsion of negatively charged mercury atoms. Thus mercury moves to the circumference from the site facing the anode, leaving a bright mercury surface at the starting area as shown in Fig. 6. This opinion is different from that of Antwelier and von Stackelberg.[16] The particles of elemental tellurium which have been desorbed and suspended in the bulk of the solution are seen moving rapidly along the surface of the mercury cathode in three types of flow according to the applied potentials, as shown in Fig. 7. Jones and Kaye[17] observed this kind of mercury movement by using a dilute suspension of coal particles.

At the potentials of the positive half of the maximum, the brown mist has an umbrella shape (Fig. 7-*A*), and the surface of the mercury drop is covered with a

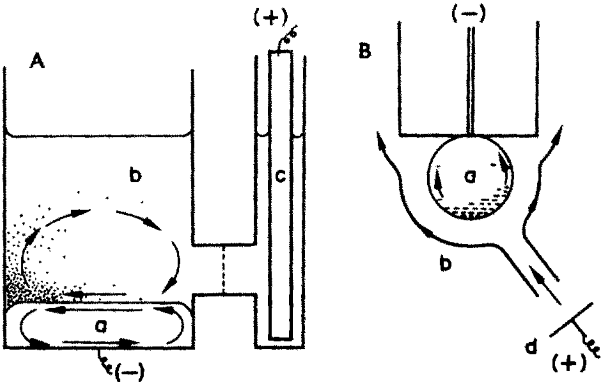


Fig. 6.—Streams of mercury and ammonium chloride solution with K_2TeO_3 at −1·4 V.

A: at the surface of a large mercury cathode
B: at the surface of a mercury drop
a: mercury pool or mercury drop
b: 1*M* NH_4Cl with K_2TeO_3
c: carbon rod anode
d: anode

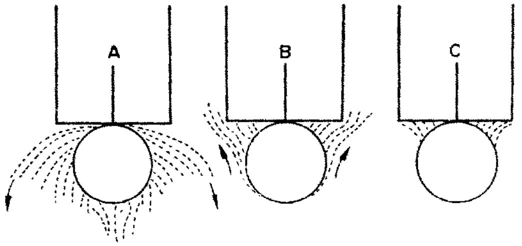


Fig. 7.—The flow of the brown mist at various potentials in the polarography of 1 m*M* K_2TeO_3 in 0·1*M* NH_4Cl–0·1*M* NH_4OH.
A, at −1·25 V; *B*, at −1·3 V (E_{max}); *C*, at −1·9 V

tellurium deposit. Especially when it is in a saturated solution of potassium chloride, the mercury drop is apparently black. As soon as the potential reaches the value of E_{max}, the brown mist begins to flow suddenly upward (Fig. 7-*B*). This phenomenon also means that the mercury surface begins to move suddenly at the potential of E_{max}. This is distinctly seen by sudden clearance of the mercury drop from black to bright metallic when it is in a saturated solution of potassium chloride. The mist of elemental tellurium is also observed at the final increase of the current (Fig. 7-*C*).

Catalytic reaction of hydrogen evolution

On increase of the negative potential of the tellurium cathode established on the mercury drop by the electrode process of Te(IV) → Te^0, hydrogen begins to evolve from the tellurium surface at the decomposition potential.

The solution side of the electric double layer at the interface of the tellurium electrode and the solution is negatively charged, and its electrostatic potential equals the work function of the solution, Φ_{sol}, less the electron affinity of tellurium, χ_{Te}. Taking Φ_{Te} as the work function of tellurium, the potential barrier which hinders electron-flow from tellurium to the solution is expressed by $\Phi_{sol} - \Phi_{Te}$. When a cathodic potential V is applied to tellurium the barrier amounts to $\Phi_{sol} - \Phi_{Te} - eV$.[14] So if this value becomes enough to give rise to the maximum, the surface of the tellurium electrode is relatively rich in electrons and has the character of telluride. According to Lingane and Niedrach[3] telluride is present as H_2Te at pH 4, and as HTe^- at $4 < pH < 11$. The adsorbed hydrogen will be very quickly reduced, as follows.

$$\begin{tikzcd}[column sep=small] \mathrm{HTe}^-_{ads} & + e^- \longrightarrow \tfrac{1}{2}\mathrm{H}_2 + & \mathrm{Te}^{2-}_{ads} \arrow[ll, bend left, "\mathrm{H}^+"] \end{tikzcd} \tag{1}$$

The Te^{2-}_{ads} thus formed again combines with hydrogen ions to form HTe^-, and so on; this cycle is repeated to evolve hydrogen catalytically. Some part of the hydrogen may reduce the electrode substrate and form HTe^- in the solution at $4 < pH < 11$ as follows.

$$\mathrm{Te}^0 + 2\mathrm{H} = \mathrm{HTe}^- + \mathrm{H}^+ \tag{2}$$

The HTe^- thus formed or telluride ion originally present gives the same cycle as in (1) and makes hydrogen evolve. The reason why the catalytic wave of hydrogen does not appear in strongly alkaline solution is that tellurium cannot exist in the elemental form but dissolves in the alkaline medium. On the other hand, some of the HTe^- either in the solution or in the adsorbed state is oxidized instantaneously to elemental tellurium by dissolved oxygen or by ultraviolet rays.

$$\begin{aligned} &\mathrm{HTe}^- \xrightarrow{h\nu} \mathrm{H}^+ + \mathrm{Te}^0 + 2e^- \\ &2\mathrm{HTe}^- + \mathrm{O}_2 + 2\mathrm{H}^+ \longrightarrow 2\mathrm{H}_2\mathrm{O} + 2\mathrm{Te}^0 \end{aligned} \tag{3}$$

Elemental tellurium thus produced forms the brown mist which appears in the vicinity of the dropping mercury surface in the potential range of the polarographic maximum.

Photochemical effect on the electrode process

Irradiation of the surface of the mercury cathode with ultraviolet light promotes the photodecomposition and increases the amount of the brown mist but decreases the height of the polarographic maximum, because of the decrease of the amount of hydrogen telluride near the electrode.

Figure 8 shows the experimental result of an "on–off" test of ultraviolet irradiation at the d.m.e. The current is higher when it is dark and lower when it is bright. This on–off effect on the maximum current begins to appear about more than half an hour after the electrolysis has been carried out at E_{max}. For this reason, it is thought that the amount of telluride near the electrode increases enough to show the effect. The small fluctuations of the current which appear in the current–time curves in Fig. 8 seem due to the lack of uniform distribution of the effective ions near the electrode. In fact, on stirring of the solution the fluctuation of current becomes very small.

The response time of the current when the light is off is shorter than when it is on. The former is within 1 sec, while the latter is within 10 secs. This suggests the necessity of above-mentioned half an hour pre-electrolysis.

On the other hand, the telluride formed on the electrode reacts in the diffusion

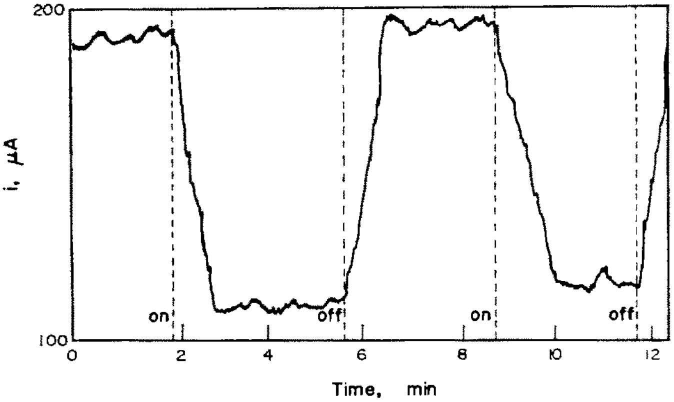


FIG. 8.—Effect of ultraviolet irradiation of d.m.e. on the catalytic current of hydrogen at constant voltage of $-1{\cdot}2$ V (E_{max}) in $1M$ NH_4Cl with $0{\cdot}15 \times 10^{-3}M$ H_2TeO_3.

layer according to equation (4):

$$2HTe^- + Te(IV) = 3Te^0 + 2H^+ \tag{4}$$

This has been reported to be the cause of the brown mist.[4,5,8] However, according to our experimental results, the brown mist appears in spite of the absence of Te(IV), especially in the case of suspension polarography of elemental tellurium powder or block polarography using an elemental tellurium block, so that the theory which needs the presence of Te(IV) is not always acceptable.

The descending branch of the maximum

At a potential where the maximum is over (region E in Fig. 1), the brown mist disappears. At still more negative potentials than E_f, however, the brown mist begins to appear again (Fig. 7C), because hydrogen telluride begins to be formed again owing to the reduction of tellurium by the nascent hydrogen produced electroreductively, *e.g.*, by $NH_4^+ + e^- \rightarrow NH_3 + H$. This flow of brown mist is more speedy than at B in Fig. 7, and it means that the movement of the mercury at C is more rapid than at B.

Because of the desorption of tellurium due to the above-mentioned mercury movement from the surface of the d.m.e., the tellurium electrode which has been established is cancelled and becomes simply a mercury cathode, so the catalytic wave of hydrogen on the tellurium electrode disappears at more negative potentials than E_{max} and at the same time i_{max} suddenly falls.

If the tellurium deposited on the mercury cathode is not desorbed at more negative potentials than E_{max}, the catalytic hydrogen wave does not vanish at any potential. The experiments shown in Figs. 3 and 4 illustrate this.

Minimum after the maximum

In the polarogram of Te(IV), a small current minimum appears at the potential immediately after the descent of the maximum (D in Fig. 1). The larger the height of the maximum, the deeper the following minimum, but it cannot be seen when the sample solution is agitated or in suspension polarography. Figure 9A shows a polarogram of Te(IV) and B shows a polarogram of the same solution, but with the potential sweep reversed. In B, the minimum at the negative side of the maximum disappears, while a new minimum appears at the positive side of the maximum. This shows that this minimum does not essentially correspond to the potential, but is a kind of after-effect of the maximum wave.

It is thought that the cause of the appearance of the minimum is the screening effect, on Te(IV) diffusion toward the electrode, of the products which remain in the vicinity of the mercury surface. These products are thought to be composed of HTe^-, H_2 *etc*, which remain near the electrode and react reductively with the Te(IV) ions [see equation (4)] to cause the temporal decrease of the current. This kind of redox reaction is suggested by Schmidt and von Stackelberg,[5] who made use of this phenomenon for the explanation of the plateaux before and after the Te(IV) maximum being at the same level of current.

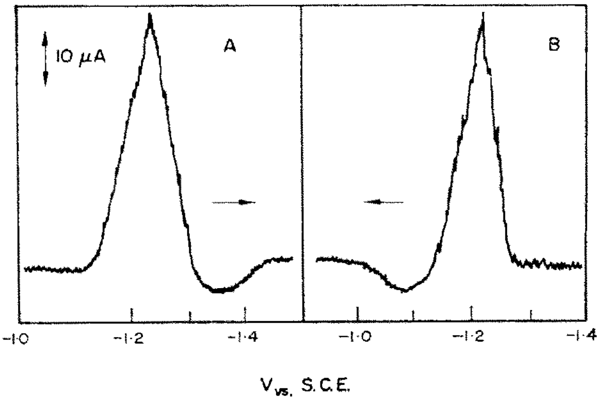


FIG. 9.—Polarograms of $0 \cdot 5 \times 10^{-3}M$ K_2TeO_3 in $1M$ NH_4Cl–$1M$ NH_4OH.
A: swept from positive to negative potential
B: swept from negative to positive potential

Current before and after the maximum

Schmidt and von Stackelberg[5] considered the problem of the plateaux before and after the Te(IV) maximum being at the same level, though the electrode process before the maximum is $Te(IV) + 4e^- \rightarrow Te^0$, while after the maximum it is $Te(IV) + 6e^- = Te^{2-}$. The apparent anomaly is explained by them in terms of telluride, formed on the electrode, reacting with Te(IV) in the diffusion layer according to equation (4), to produce tellurium. Therefore one third of the Te(IV) concentration in the diffusion layer is cancelled to make the $n = 6$ process look like an $n = 4$ process.

On the other hand, according to our experimental results, in spite of the absence of Te(IV), especially in the case of the suspension polarography of elemental tellurium powder or the block polarography using an elemental tellurium block, the currents before and after the maximum are equal. In the case of the polarography of Te(IV), the reduction proceeds in steps $Te(IV) \xrightarrow{4e^-} Te^0_{ads} \xrightarrow{H_2} HTe^- + H^+$. After the reduction of $Te(IV) \rightarrow Te^0$, the processes on the d.m.e. are as explained above by equations (1), (2) and (3). Even if elemental tellurium could adhere to the mercury electrode at a potential more negative than the peak potential of the maximum, it produces hydrogen to reduce itself to telluride. Consequently, since the latter half-step $Te^0 \rightarrow HTe^-$ is not faradaic, it shows no current, while the first half-step gives a current corresponding to n as high as 4. In the case of strongly alkaline medium, reductively produced elemental tellurium is successively dissolved in the medium as alkali metal polytelluride at potentials more positive than the maximum, while at the more negative potentials the polytelluride is reduced to simple telluride, showing a reductive current higher than in the mild alkaline medium, as shown in Fig. 10*b*.

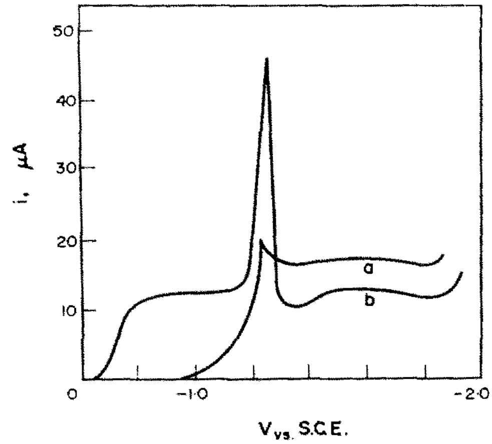


FIG. 10.—Polarograms of $1 \times 10^{-3}M$ K_2TeO_3 in (*a*) $1M$ KOH; (*b*) $0{\cdot}1M$ NH_4Cl–$0{\cdot}1M$ NH_4OH.

Schmidt and von Stackelberg,[5] like Norton, Stoenner and Medalia[9] reported that in the case of the Te(VI) wave the reduction ($n = 8$) leading to Te^{2-} is modified ($n = 6$) by the side-reaction of Te(VI) with Te^{2-} in the diffusion layer. We do not agree with this opinion, however, for the same reason as in the case of Te(IV). Here the reduction $Te(VI) \rightarrow Te^0$ ($n = 6$) provides the net current after the maximum. This supports the result reported by Issa *et al.*[10]

POSSIBILITIES OF ANALYTICAL APPLICATION

On the basis of the results of this survey of the tellurium maximum, we can list the analytical possibilities, though further examination is necessary.

1. The peak-height of the maximum is linearly proportional to the concentration of Te(IV) in the regions of $0{\cdot}5$–$1{\cdot}0 \times 10^{-3}M$ and $1{\cdot}0$–$1{\cdot}5 \times 10^{-3}M$. Though these two regions are adjacent, the slopes of the curves are different, so calibration curves are necessary.

2. Qualitative analysis for tellurium in insoluble form, *e.g.*, Te, TeO_2, H_2TeO_3, or $(NH_4)_2TeO_3$, can be carried out by suspension polarography or by block polarography. By suspension polarography the relative concentration of the powder could be found semiquantitatively.

3. For the determination of tellurium, the amperometric application of the maximum current seems to be more sensitive and specific than measurement of the $Te(IV) \rightarrow Te^0$ wave.

4. The photochemical effect on the maximum current of tellurium can be utilized for the "on–off" indication of ultraviolet light.

5. The maximum current for tellurium can be utilized for indication of the contact of mercury with tellurium.

6. Besides the usual constancy of analytical conditions needed in polarography, the illumination of the laboratory should also be kept constant, because of the photochemical effect on the electrode process corresponding to the current maximum.

Besides the surface-active substances shown in Fig. 2, ultraviolet irradiation of the electrode is effective to some extent for the suppression of the maximum in order to obtain a better background for analysis.

Zusammenfassung—Das Polarogramm von Tellur(IV) in schwach alkalischer Lösung hat im Diffusionsstrom-Plateau ein scharfes Maximum. Der dieses Maximum hervorrufende Elektrodenprozeß wurde auf verschiedene Weise untersucht; mit Hilfe der Halbleiterkatalyse, der "Block"-Polarographie und ultravioletter Bestrahlung der Quecksilbertropfelektrode. Es wurde gefunden, daß das Maximum durch die katalytische Stufe des Wasserstoffs verursacht wird, der durch das auf der Quecksilberoberfläche abgeschiedene Tellur freigesetzt wird. Ein Teil des Tellurs wird durch den katalytisch gebildeten naszierenden Wasserstoff zu Tellurwasserstoff reduziert. Der gewöhnlich in der Nähe der Oberfläche der Quecksilbertropfelektrode auftretende braune Nebel besteht aus elementarem Tellur, das durch Zersetzung von Tellurwasserstoff entsteht. Der plötzliche Abfall des Stroms bei negativerem Potential als dem des Strommaximums beruht auf Tellurdesorption, die durch die Bewegung des Quecksilbers bedingt ist.

Résumé—Le polarogramme du tellurium(IV) en solution faiblement basique a un maximum accentué sur le palier de courant de diffusion. On a examiné le processus à l'électrode qui provoque ce maximum au moyen de diverses techniques telles que la catalyse au semi-conducteur, la polarographie de "blocage" et l'irradiation ultra-violette de l'électrode à goutte de mercure. On a trouvé que le maximum est causé par la vague catalytique de l'hydrogène produit par le tellurium déposé sur la surface du mercure. Une partie du tellurium est réduite en hydrogène telluré par l'hydrogène naissant formé catalytiquement. Le brouillard brun qui apparaît habituellement au voisinage de la surface de la cathode à goutte de mercure se compose de tellurium élémentaire produit par la décomposition de l'hydrogène telluré près de l'électrode. La chute brusque dans le maximum du courant à un potentiel plus négatif que le potentiel du pic du maximum est dûe à la désorption du tellure, causée par le mouvement du mercure.

REFERENCES

1. L. Schwaer and K. Suchy, *Collection Czech. Chem. Commun.*, 1935, **7**, 25.
2. J. J. Lingane and L. W. Niedrach, *J. Am. Chem. Soc.*, 1948, **70**, 4115.
3. *Idem*, *ibid.*, 1949, **71**, 196.
4. W. Hans and M. von Stackelberg, *Z. Elektrochem.*, 1950, **54**, 62, 65.
5. H. Schmidt and M. von Stackelberg, *J. Polarog. Soc.*, 1962, **8**, 49.
6. L. B. Reznik and P. N. Kovalenko, *Zh. Fiz. Chim.*, 1965, **40**, 489.
7. S. I. Zhdanov and R. G. Pats, *Elektrokhimiya*, 1965, **1**, 947.
8. R. A. Jamieson and S. P. Perone, *J. Electroanal. Chem.*, 1969, **23**, 441.
9. E. Norton, R. W. Stoenner and A. I. Medalia, *J. Am. Chem. Soc.*, 1953, **75**, 1827.
10. I. M. Issa, S. E. Khalafalla and R. M. Issa, *Rec. Trav. Chim.*, 1956, **75**, 1105.
11. S. I. Zhadanov and R. G. Pats, *Elektrokhimiya*, 1965, **1**, 1092.
12. M. Shinagawa, H. Nezu, A. Muromatsu and N. Yano, *Rev. Polarog. Japan*, 1967, **14**, 118.
13. *Idem*, *ibid.*, 1968, **15**, 108.
14. M. Shinagawa, N. Yano and H. Nezu, *ibid.*, 1970, **16**, 120.
15. J. Kuta and I. Smoler, *Progress in Polarography*, eds. P. Zuman and I. M. Kolthoff, Vol. I, p. 43. Interscience, New York, 1962.
16. M. von Stackelberg, H. J. Antweiler and L. Kieselbach, *Z. Elektrochem.*, 1938, **44**, 663.
17. L. F. Jones and R. C. Kaye, *J. Electroanal. Chem.*, 1969, **20**, 213.

Talanta, 1972, Vol. 19, pp. 451 to 464. Pergamon Press. Printed in Northern Ireland

SEPARATION AND DETERMINATION OF RUTHENIUM BY EVOLUTION WITH CHROMIUM(VI)-CONDENSED PHOSPHORIC ACID REAGENT*

TOSHIYASU KIBA®, KIKUO TERADA, TOMOE KIBA and KAZUO SUZUKI
Laboratory for Analytical Chemistry, Department of Chemistry, Faculty of Science,
Kanazawa University, Marunouchi-1, Kanazawa, Ishikawa Pref., Japan

(*Received* 7 *June* 1971. *Accepted* 7 *October* 1971)

Summary—Ruthenium in various chemical forms can be evolved as the tetroxide from insoluble matrix materials by heating the sample with chromium(VI)-condensed phosphoric acid reagent (abbreviated as Cr(VI)-CPA). Because of its excellent decomposing power for various solid samples, condensed phosphoric acid is very useful in the chemical analysis of various insoluble materials, and when an oxidizing agent such as potassium dichromate is added in the CPA medium, drastic oxidation proceeds on heating. This method is now extended to the separation of ruthenium from marine sediments. During the reaction with Cr(VI)-CPA ruthenium tetroxide is evolved and collected in an absorbent solution of 6*M* hydrochloric acid and ethanol (1:1), and the ruthenium is then determined spectrophotometrically with thiourea or radiometrically by counting the β- or γ-activity. Osmium, which can be evolved as the tetroxide by the same treatment, can be eliminated beforehand by heating the sample with Ce(IV)-CPA, which removes osmium but not ruthenium. The successive distillations by means of Ce(IV)-CPA and Cr(VI)-CPA give satisfactory results for the separation between osmium and ruthenium. This method might be useful for the separation of ruthenium in geochemical or neutron-activation analysis.

SINCE 1951 Toshiyasu Kiba and his co-workers[1] have worked on development of a new chemical treatment for decomposition of various solid samples by use of condensed conc. phosphoric acid. The so-called condensed phosphoric acid (abbreviated as CPA) is also called dehydrated phosphoric acid, strong phosphoric acid or polyphosphoric acid, and prepared by dehydration of commercial orthophosphoric acid or the hydration of phosphorus pentoxide. This anhydrous material is a mixture of various kinds of phosphoric acid such as ortho-, pyro-, tri-, tetra-, and so on, the P_2O_5 content being generally $>72{\cdot}4\%$. The composition of the CPA depends on the temperature used for the dehydration.[2] In this study the CPA used was prepared by heating reagent grade orthophosphoric acid to 300°. It is a stable and inactive viscous liquid at room temperature, but heated it loses its viscosity and becomes very reactive. By simple heating with CPA, powdered glasses, insoluble silicates,[3,4] alumina,[5] clays,[5] and insoluble sulphates[6] can be decomposed readily, giving a transparent or slightly turbid liquid. Furthermore, when an oxidizing agent such as potassium iodate or potassium dichromate is added with CPA to various inorganic or organic samples, a drastic oxidation reaction occurs along with the decomposition of the sample, and some resistant samples such as elemental carbon,[7] graphite,[8] and powdered coal[9] can be decomposed easily, *e.g.*, with the evolution of carbon dioxide and iodine equivalent to the oxygen consumed when KIO_3-CPA is used. Simple organic and biochemical compounds can be decomposed with oxidant-CPA with

---

* A part of this work was performed at the Research Reactor Institute, Kyoto University.

accompanying evolution of carbon dioxide, nitrogen, and halogen, depending on the composition of the sample. On the other hand, a reducing CPA medium has been prepared by heating a mixture of tin(II) chloride dihydrate and CPA to 300° to expel water and hydrogen chloride from the medium. This is called Sn(II)–CPA and can be stored in contact with the atmosphere without any loss of its reducing power. When samples containing sulphur, such as insoluble sulphates, sulphide ores and organic sulphur compounds, are heated with Sn(II)–CPA, hydrogen sulphide is evolved quantitatively. Hydrogen selenide and mercury can also be evolved from samples containing selenium and mercury by heating with Sn(II)–CPA. Thus, new sample treatment with various CPA systems has been developed and the method is highly popular in Japan, more than fifty articles having appeared on chemical analysis with the use of CPA, some of which are listed in Table I. In appreciation of this work the Japan Society for Analytical Chemistry awarded the Society Prize in 1963 to Prof. Toshiyasu Kiba. It must be noted that CPA is not only useful for analytical purposes but also for organic synthesis[10] and electrochemical investigations[11,12] in anhydrous media. The unusual reactivity of ordinary oxidants and reductants in CPA media has been exploited by Gopala Rao and his collaborators.[13]

A further application is in establishment of a simple method for ruthenium in marine sediments with use of CPA, since this element has never been examined in CPA medium. The ruthenium should be oxidized to Ru(VIII) and evolved as the

TABLE I.—CPA MEDIA APPLIED IN CHEMICAL ANALYSIS

Sample	Determinand	Treatment by	Gas evolved	Determination method	Reference
Uranium dioxide	U(VI)	CPA		polarography	14
Thorium dioxide	B	CPA		colorimetry	15
Graphite	C	KIO_3–CPA	CO_2 iodine	iodometry	7, 8
Organic compds.	oxid. value	KIO_3–CPA	CO_2 iodine	iodometry	16
Organic compds.	C	KIO_3–CPA	CO_2 iodine	alkalimetry	17
Tungsten metal	C	KIO_3–CPA	CO_2	alkalimetry	18
Organic compds.	N	KIO_3–CPA	nitrogen	gas volumetric	19
Nitrate	N	KIO_3–CPA	nitrogen	gas volumetric	20
Biolog. materials	N	KIO_3–CPA	nitrogen	gas volumetric	21
Teeth, hair	N	KIO_3–CPA	nitrogen	gas volumetric	22
Halides	halogen	$K_2Cr_2O_7$–CPA	halogen	iodometry	23
Polyvinyl chloride	S	$K_2Cr_2O_7$–CPA	decomposition of sample		24
Coal powder	Ge	$K_2Cr_2O_7$–CPA	decomposition of sample		9
Sulphate	S	Sn(II)–CPA	H_2S	iodometry	6
Sulphide ores	S	Sn(II)–CPA	H_2S	iodometry	25
Thiocyanates					
Sulphite					
Alumina, clay	S	Sn(II)–CPA	H_2S	iodometry	5
Organic compds.	S	Sn(II)–CPA	H_2S	colorimetry	26
Iron and steels	S	Sn(II)–CPA	H_2S	colorimetry	27
Ash of polypropylene	S	Sn(II)–CPA	H_2S	colorimetry	28
Protein	S	Sn(II)–CPA	H_2S	colorimetry	26
Spun rayon	S	Sn(II)–CPA	H_2S	colorimetry	29
Pesticides	Hg	Sn(II)–CPA	Hg	colorimetry	30
Sulphide ores	Se	Sn(II)–CPA	H_2Se, Se	colorimetry	31

gaseous tetroxide from the matrix. After various experiments Cr(VI)–CPA was preferred for this purpose. Osmium was found to behave similarly to ruthenium with Cr(VI)–CPA, but another CPA medium, Ce(IV)–CPA, was found to separate osmium from ruthenium by evolving only osmium tetroxide. Separation by evolution of gaseous inorganic compounds has been described by Sandell,[32] especially for metal chlorides, but these processes are based on evolution from aqueous solution, not from a solid sample. Although ruthenium has been separated by distillation by heating an acidic solution containing various oxidizing agents, a tedious treatment of a solid sample by fusion and dissolution with acids must be done first.[33] The present method can be directly applied to soil samples without fusion or dissolution of the samples, and ruthenium in various chemical forms can be distilled as tetroxide by only one or two operations. Ruthenium and osmium are apt to be lost during the usual operations of distillation and fusion in acidic media, but this CPA treatment can be applied in a closed system from the start of the analytical process without any loss of the elements.

EXPERIMENTAL

Reagents

Condensed phosphoric acid (CPA). Place 300–400 g of commercial orthophosphoric acid of extra pure reagent grade in a 300-ml conical beaker, and dehydrate it by heating on a 500-W electric heater until a thermometer dipped in the liquid indicates 300°. During the heating the vapour coming off should be rapidly removed from the neighbourhood of the liquid surface through a glass tube, one end of which is held near the liquid surface, the other end being connected to a suction pump. Continue the suction until no further vapour emerges. The sirupy liquid thus obtained should be stored in a closed vessel.

Ruthenium standard solution. Dissolve ruthenium(III) trichloride monohydrate in $2M$ hydrochloric acid. Standardize the solution gravimetrically as follows: take an aliquot of the solution and dilute it to about $1M$ in hydrochloric acid. Then precipitate metallic ruthenium with magnesium metal powder and gentle heating. Add just enough concentrated hydrochloric acid to dissolve the excess of magnesium metal, and heat gently to coagulate the precipitate. Filter off the precipitate with a filter stick and glass-fibre filter paper. Wash with hydrochloric acid, ethanol and ether, successively, and dry at room temperature for 2 hr under reduced pressure, and weigh.

Osmium standard solution. Dissolve osmium tetroxide in $0{\cdot}2M$ sodium hydroxide solution. Standardize the solution volumetrically by Klobbie's method:[34] add potassium iodide to the osmium tetroxide in dilute sulphuric acid and titrate the liberated iodine with standard sodium thiosulphate solution potentiometrically.

Thiourea solution, 10%.

Other chemicals. Potassium dichromate, cerium (IV) sulphate, hydrochloric acid and sodium hydroxide, all of extra pure grade, were used without further purification. Doubly distilled water was used except for the radiochemical processes.

Radioactive tracer. Ruthenium-106 as trichloride from The Radio Chemical Centre, England, and osmium-185 as osmates prepared by sodium peroxide fusion of irradiated osmium metal in the Research Reactor Institute, Kyoto University, were employed as tracers to examine the behaviour of the two elements in the course of the reaction with CPA.

Apparatus

Radioactivity measurements. EA-14 NaI(Tl) crystal of well-type, scaler SA-250 and timer TM-2, all from Kobe Kogyo Co., for γ-counting. Multichannel pulse-height analysers, EDS-34208, Toshiba Co., (200 channels) and RCL (512 channels); Ge(Li)-detector, ORTEC Model 8100-45, having a resolution of about 2·5 keV for the 1333-keV gamma-peak of ^{60}Co; gas-flow counter (ALOKA LBG-21 U, Nippon Irigaku Co.).

Reaction vessel and absorbing tubes. The apparatus used is shown in Fig. 1; the reaction vessel (A) and absorbing tubes (B) are connected together by ground-glass ball-joints. The reaction vessel is a round-bottomed flask having a glass cap fitted to its top and provided with inlet and outlet tubes. A glass tube closed at one end is inset in the cap to take a thermometer for measuring the temperature of the reaction medium. A few drops of silicone oil are put in the tube to reduce the time-lag of temperature indication.

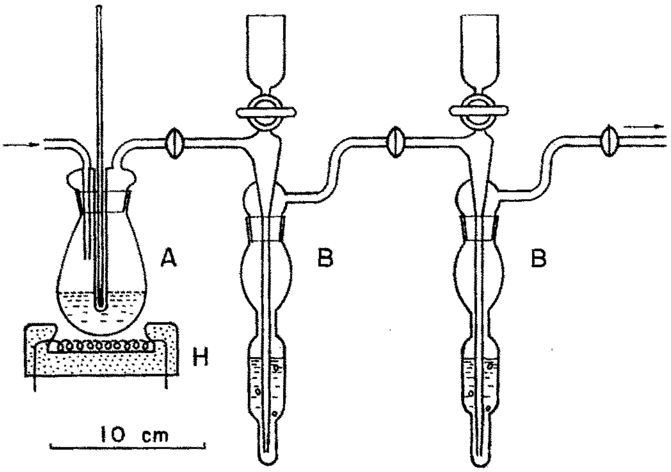


FIG. 1.—Reaction vessel (A), absorbing tubes (B) and electric heater (H).

Samples

Test solutions. To establish generally useful procedures ruthenium and osmium compounds in various chemical forms were submitted to test. Radioactive tracers of the two elements were also employed to estimate recovery and separation factor.

Sample to be analysed. Marine sediment was preferred for the study on the environmental radioactive contamination of the Japan Sea. The samples were parts of cores taken from the bottom of the Japan Sea, and surface sediments from Nanao Bay near Kanazawa, and their locations are shown in Table VI.

Experimental procedure

Place a sample solution in the reaction vessel and add a few drops of dilute sodium hydroxide solution to keep the solution alkaline. Evaporate the solution to dryness on a water-bath. Add about 20 g of CPA and 1–4 g of cerium(IV) sulphate; put 10 ml of the absorbing solution [9 ml of a mixture of 6*M* HCl and C_2H_5OH (1:1 v/v), plus 1 ml of 10% thiourea solution] into each of the absorbing tubes. Then connect all the joints as shown in Fig. 1. Suck the air slowly from the last outlet tube with a suction pump and heat the reaction vessel with an electric heater to start the reaction. The time needed to complete the oxidation and distillation is that needed to raise the temperature to that appropriate for osmium. After the distillation, stop the heating and disconnect all the connections. Combine the absorbing solutions in a 25- or 50-ml standard flask, together with the washings and dilute to the mark with a 1:1 v/v mixture of 6*M* hydrochloric acid and ethanol. Measure the absorbance of the red solution at 480 nm. Determine the osmium content from a working curve pre-prepared in the same way with a series of solutions of osmic acid. For tracer work, gamma-count a portion (usually 3 ml) of the absorbing solution.

After the separation of osmium as described above put about 2 g of potassium dichromate (in 2 or 3 portions) into the reaction vessel, which must be cooled to below 100° after the osmium distillation. Heat and cool the vessel whenever the reagent is added, to make the dissolution of the reagent uniform in the CPA medium. Distil the ruthenium by heating the reaction vessel to 240° The absorbing solution is 1:1 v/v 6*M* hydrochloric acid and ethanol mixture. After distillation transfer the absorbing solution into a standard flask together with the washings and dilute to volume. For spectrophotometric determination of ruthenium, use the thiourea method. In a 25-ml flask take an aliquot of the solution, add 1 ml of 10% thiourea solution and dilute to just below the mark with the mixed hydrochloric acid–ethanol solution. Stand the vessel for 10 min at 85° in a water-bath to develop the colour. Cool, dilute to the mark with acid–ethanol mixture, and measure the absorbance of the blue solution at 620 nm. Determine the ruthenium content from a working curve prepared by the same spectrophotometric procedure with a series of solutions of ruthenium chloride. The colour is very stable.[35]

For the tracer method use a portion (usually 3 ml) of the absorbing solution for γ-counting.

When marine sediments are to be analysed the sample should be dried at 110° for an hour and ground in a mortar, and a 1-g portion should be used in the reaction vessel. The analytical procedure is the same as for solutions.

RESULTS AND DISCUSSION

Distillation recovery of ruthenium

The choice of a suitable oxidizing agent useful in the CPA decomposition and distillation method was the first problem. Various oxidizing agents were tested according to the procedure described above, and the amount of ruthenium distilled was determined spectrophotometrically in each case. The recovery of ruthenium by various oxidizing agent–CPA treatments is shown in Table II, from which potassium dichromate is found the most useful for the purpose. Cerium(IV) sulphate was found not to react with ruthenium, and ruthenium tetroxide did not appear at all in the absorbing solution. This fact shows that potassium dichromate acts more powerfully than cerium(IV) sulphate in CPA, in contrast to the order of their oxidation potentials in aqueous solution. This result is compatible with that obtained by Rao for the formal redox potentials in phosphoric acid of increasing concentrations.[36] This reversal of the redox potential order in CPA may be attributed to the strong complex-forming behaviour of chromium(III) with CPA. The ideas of Charlot[37] on acid-base equilibrium involving oxide complexes in a melt may be extended to the reaction in CPA, a non-aqueous medium resembling a melt.

TABLE II.—RECOVERY OF RUTHENIUM WITH VARIOUS CPA REAGENTS

Oxidizing agent	g/20 g of CPA	Recovery of Ru,* %
Potassium dichromate	1	101·9
	1	98·6
	1	100·3
Potassium periodate	1	77·0
	1	87·8
	1	84·0
Calcium hypochlorite	1	11·2
Potassium iodate	1	0
Potassium persulphate	1	0
Cerium(IV) sulphate	1	0
	4	0
Hydrogen peroxide, 30%	2 ml	0

* ($1{\cdot}69_8$ mg of Ru, taken as $RuCl_3$).

$$Cr_2O_7^{2-} + 6e^- \rightleftharpoons 2\,Cr^{3+} + 7\,O^{2-}$$

The equilibrium potential is

$$E = E_0 + \frac{RT}{nF}\log\frac{[Ox]}{[Red]} - \frac{RT}{nF}\log\,[O^{2-}]$$

In this equation, if an O^{2-} acceptor exists in the system, $[O^{2-}]$ decreases and the value of E should therefore be higher. CPA is itself an O^{2-} acceptor with the equilibria

$$P_2O_7^{4-} + O^{2-} \rightleftharpoons 2PO_4^{3-}$$

$$P_3O_{10}^{5-} + 2O^{2-} \rightleftharpoons 3PO_4^{3-}$$

Hence, an apparently anomalous formal redox potential may occur for chromium (VI) and cerium(IV).

The recovery of ruthenium from ruthenium(III) chloride by distillation from Cr(VI)–CPA was achieved as described above, and further examination for other ruthenium compounds was tried as follows. Standard ruthenium chloride solution was put in the reaction vessel and sodium hydroxide solution, sodium sulphide solution or magnesium powder was added. Thus the ruthenium was transformed into the hydroxide, sulphide, or the metal. After evaporation of the contents to dryness, the Cr(VI)–CPA treatment was applied. The time required for completion of reaction was examined by changing the absorbing solution for fresh at intervals of several minutes. The results are shown in Fig. 2. The chloride was the most easily decomposed, taking only about 5 min, but sulphide and metallic ruthenium were somewhat resistant, since it took about 30 min to complete the distillation of ruthenium tetroxide. In this case chromium(VI) dioxychloride was also sometimes evolved from the chloride-rich sample, but it caused no interference with the determination of ruthenium.

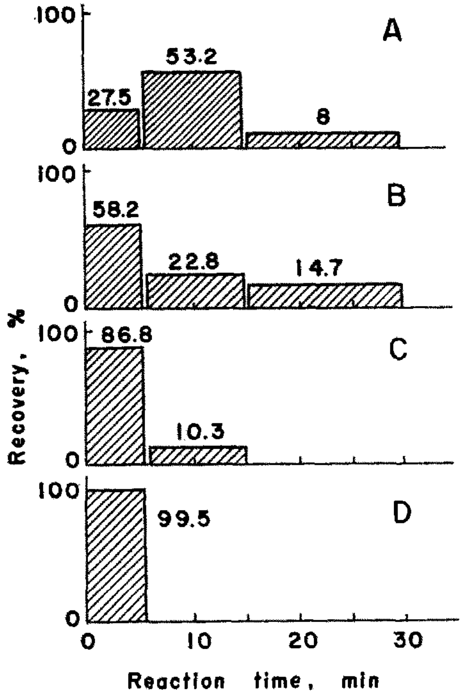


FIG. 2.—Recovery of RuO$_4$ during the Cr(VI)–CPA treatment.
Sample: (A) Ru metal, (B) Ru$_2$S$_3$, both with 2 g of K$_2$Cr$_2$O$_7$ in 20 g of CPA; (C) Ru(OH)$_3$, (D) RuCl$_3$, both with 1 g of K$_2$Cr$_2$O$_7$ in 20 g of CPA.

Distillation recovery of osmium

Osmium was distilled along with ruthenium on treatment with Cr(VI)–CPA, but was even more readily distilled from mixtures of weaker oxidizing agents with CPA. To find a suitable CPA system to separate osmium from ruthenium, the recovery of osmium by distillation from various reagent–CPA systems was examined, using osmium samples in various forms. Spectrophotometric and radioisotopic tracer methods were used. The results are summarized in Table III, from which it is seen

TABLE III.—RECOVERY OF OSMIUM WITH VARIOUS CPA REAGENTS

Oxidizing agent added in CPA	g/20 g of CPA	Osmium as	Amount of Os, *mg*	Recovery *mg*	Recovery %
Potassium persulphate	1	Os	$1{\cdot}20_7$	$1{\cdot}07_1$	88·7
	2	Os	$0{\cdot}24_1$	$0{\cdot}05_5$	22·8
	2	OsS_2	$0{\cdot}24_1$	$0{\cdot}08_0$	33·2
	2	OsO_4	$0{\cdot}24_1$	$0{\cdot}08_4$	35·0
Hydrogen peroxide, (30%)	2 ml	Os	$0{\cdot}24_1$	$0{\cdot}21_9$	90·8
	3	OsS_2	$0{\cdot}24_1$	$0{\cdot}10_6$	44·0
	4	OsO_4	$0{\cdot}24_1$	$0{\cdot}18_6$	77·2
Cerium(IV) sulphate	2	Os	$1{\cdot}20_7$	$1{\cdot}26_7$	105
	4	OsS_2	$0{\cdot}24_1$	$0{\cdot}25_3$	105
	2	$Os(OH)_4$	$1{\cdot}20_7$	$1{\cdot}22_4$	101·4
	4	OsS_2	$0{\cdot}24_1$	$0{\cdot}23_7$	98·1*
	2	OsS_2	$0{\cdot}12_1$	$0{\cdot}11_4$	94·1*
	2	Os	$0{\cdot}24_1$	$0{\cdot}24_7$	102·5*
	2	Os	$0{\cdot}12_1$	$0{\cdot}12_0$	99·5*

Osmium in different chemical forms was prepared in the same way as for ruthenium.

* Radioactive tracer, ^{185}Os, was added as osmates, and the recovery was estimated by counting the activity.

that osmium can be distilled quantitatively by means of Ce(IV)–CPA in all cases. Of the oxidizing agents used, hydrogen peroxide seems to be rather useful for the purpose when it is added in a series of small portions, but its 30% solution brings a significant amount of water into the anhydrous CPA system and the temperature is considerably lowered and there is bumping of the reaction-vessel contents. Hence this reagent cannot be recommended for the CPA treatment.

Temperature control

Precise temperature control during the process was not necessary, as the temperature was simply raised from room temperature to the uppermost appropriate to each CPA reagent. Decomposition of samples and distillation of the tetroxides proceeded with the rise in temperature and was complete by the time the temperature reached its highest point. Therefore additional heating or extended heating time should be avoided since the CPA is apt to solidify if the temperature rises over 300°. In Table IV the recovery of ruthenium and osmium is given as a function of temperature. From these results it is also seen that ruthenium is not evolved at all by Ce(IV)–CPA treatment.

Behaviour of other elements

Elements having chlorides which are believed to be vaporized from their acidic solutions by heating[32] were submitted to the CPA treatment. Among them Fe(III), Mn(II), Sn(II, IV), Sb(III, V), Te(VI), Re(VII), and Ir(IV) could not be found in the distillate. Halogen gas was evolved from halides, and selenium, mercury, technetium, and arsenic have a tendency to yield gaseous compounds. By the use of tracers it was found that about 30–40% of selenium(VI), 10–20% of mercury(I, II) and 0–2% of arsenic(III) was lost from samples containing 10 mg of each element, on treatment with Cr(VI)–CPA. Technetium(VII) in tracer amounts lost 10–20% to the distillate after the same treatment. When the Ce(IV)–CPA treatment was used before the Cr(VI)–CPA treatment, the elements that could be volatilized were all removed by the former

TABLE IV.—RECOVERY OF OSMIUM AND RUTHENIUM AT VARIOUS TEMPERATURES OF THE CPA MEDIA

Oxidizing agent (g/20 g of CPA)	Temperature, °C	Recovery after distillation,* % Os	Ru
Cerium(IV) sulphate (4)	210	60–70	0
	250	85–90	0
	280	98–99	0
	285	99	0
Potassium dichromate (2)	180		95
	210		99
	230		100
	240		100

* Ten milligrams of ruthenium and osmium.

treatment, and hence did not appear in the absorbing solution of the second distillation with Cr(VI)–CPA. Thus ruthenium could be separated quantitatively without contamination except that it was unavoidable that some chromium was transferred as chromium dioxychloride into the absorbing solution when chloride was present in the sample.

Successive distillations for osmium and ruthenium

Successive distillations were tried for synthesized samples containing the two elements. A mixed solution was placed in the reaction vessel, and tracers were added if necessary. An appropriate reagent to produce the desired chemical compounds of the elements was added as described in the case of ruthenium. The sample was evaporated to dryness on a water-bath, and 20 g of CPA and 1–4 g of cerium(IV) sulphate were added. The first distillation was done with the osmium absorbing solution in the absorber. Then the reaction vessel was cooled to below 100°, the ruthenium absorbing solution substituted for the osmium absorbent, 1–2 g of potassium dichromate added to the reaction vessel, and the second distillation started. The amount of the element in the absorbing solution after each distillation was determined by spectrophotometry or by γ-counting of the tracer. The results in Table V show the advantage of this CPA method. In Fig. 3 the γ-spectra of the Ce(IV)–CPA and Cr(VI)–CPA distillates, and of the residual CPA in the original reaction vessel are shown together to verify the separation. Identical spectra were obtained, not only with tracers but also with a few milligrams of carriers; hence separation by successive distillation was achieved successfully, with good recoveries of both tracers and carriers.

Separation and determination of ruthenium-106 *in marine sediment*

The separation and determination of ^{106}Ru, a fission-product nuclide, in marine sediment samples from the Japan Sea was tried by the proposed method. A 1-g sample was taken in the reaction vessel and a ruthenium chloride carrier solution containing 15 mg of ruthenium was added. The sample mixture was dried on a water-bath and subjected to successive distillation as described above. The final absorbing solution after the Cr(VI)–CPA treatment was transferred to a beaker and diluted with water to be about 1*M* in hydrochloric acid. Magnesium powder was then put in to reduce Ru(III) to Ru(0), followed by heating to coagulate the precipitate. The excess of magnesium was dissolved by dropwise addition of the minimum of concentrated hydrochloric acid required, and the solution was heated gently. The ruthenium metal

TABLE V.—RECOVERY OF OSMIUM AND RUTHENIUM AFTER SEPARATION BY SUCCESSIVE DISTILLATIONS WITH Ce(IV)–CPA AND Cr(VI)–CPA

Chemical form of sample	Taken, *mg*		Found, *mg*		Recovery, %	
	Os	Ru	Os, by Ce(IV)–CPA	Ru, by Cr(VI)–CPA	Os	Ru
Metal	$0{\cdot}24_1$	$1{\cdot}69_8$	$0{\cdot}25_0$	$1{\cdot}69_1$	103·8	98·4
	$0{\cdot}24_1$	$0{\cdot}42_5$	$0{\cdot}24_0$	$0{\cdot}42_1$	99·5	99·2
	$0{\cdot}48_2$	$0{\cdot}34_0$	$0{\cdot}50_6$	$0{\cdot}34_5$	105·0	101·6
	$1{\cdot}20_7$	$0{\cdot}34_0$	$1{\cdot}19_5$	$0{\cdot}34_3$	99·0	101·1
	tracer	$1{\cdot}69_8$	—	—	99·0*	—
	$0{\cdot}12_1$	$0{\cdot}34_0$	$0{\cdot}11_8$*	—	97·8*	—
	tracer	tracer	—	—	—	96·6*
	$0{\cdot}24_1$	$0{\cdot}34_0$	$0{\cdot}24_5$*	0.34_4*	101·8*	101·4*
Sulphide	$0{\cdot}24_1$	$1{\cdot}69_8$	$0{\cdot}24_5$	$1{\cdot}65_7$	101·5	97·6
	$0{\cdot}24_1$	$0{\cdot}42_5$	$0{\cdot}23_9$	$0{\cdot}42_4$	99·2	99·8
	tracer	$1{\cdot}69_8$	—	—	100·3*	—
	$0{\cdot}24_1$	$0{\cdot}34_0$	$0{\cdot}24_3$*	—	100·8*	—
	$0{\cdot}12_1$	$0{\cdot}34_0$	$0{\cdot}12_4$*	—	100·4*	—
	$0{\cdot}24_1$	$0{\cdot}34_0$	—	$0{\cdot}34_0$	—	100·0
	tracer	tracer	—	—	—	96·8*
	$0{\cdot}24_1$	$0{\cdot}34_0$	$0{\cdot}25_1$*	$0{\cdot}35_5$*	104·4*	104·5*

To estimate the recovery, spectrophotometric determination of both elements was employed, except where shown by an asterisk (which denotes radiometric counting).

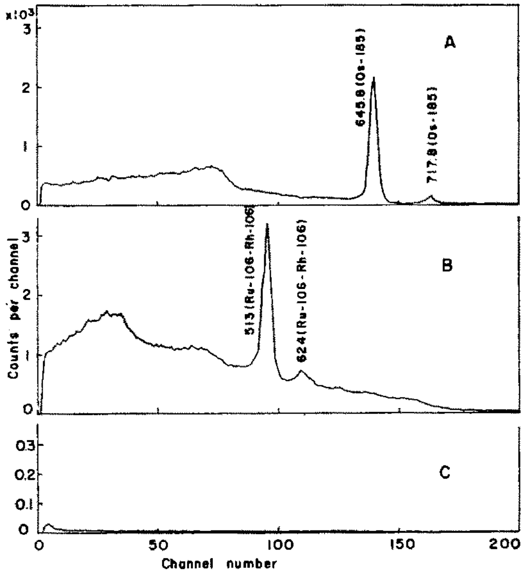


FIG. 3.—γ-Spectra of each fraction after the separation by CPA-method, determined by NaI(Tl) scintillator with 200-channel analyser.
(A) Os-fraction, (B) Ru-fraction, (C) distillation residue.

thus obtained was collected on a glass fibre filter paper on a filter stick and washed several times with hydrochloric acid, ethanol and ethyl ether, successively. The precipitate was dried at room temperature for two hours under reduced pressure, and weighed. The recovery of ruthenium carrier was estimated as the ratio of this weight to that added to the sample. Thereafter, the precipitate was wrapped with a thin film of Mylar or Kurehalon (a commercial polyethyleneterephthalate product) and additionally with aluminium foil (75 μg/mm^2) to cut off the weak β-ray generated from ^{106}Ru. The β-ray from the daughter nuclide ^{106}Rh was counted. The content of ^{160}Ru in the sediment was evaluated in the usual way.

The efficiency of the counter was estimated by counting a ^{90}Sr–^{90}Y standard. The results are shown in Table VI, where the values obtained are in fair agreement with those obtained by a method involving fusion of the solid sample with sodium peroxide, solvent extraction of ruthenium tetroxide into carbon tetrachloride, back-extraction into an aqueous phase, precipitation of metallic ruthenium with magnesium, and weighing of the carrier before the counting of the radioactivity.

TABLE VI.—RUTHENIUM-106 IN MARINE SEDIMENTS FROM THE JAPAN SEA

No.	Sample location (sample number)		^{106}Ru *pCi/g*
1	Nanao Bay,	North Bay (29)	$2{\cdot}7_6 \pm 0{\cdot}1_1$ $(3.0 \pm 0{\cdot}1)^*$
2		North Bay (22)	$4{\cdot}0_3 \pm 0{\cdot}2_4$
3		South Bay (44)	$4{\cdot}0_8 \pm 0{\cdot}1_7$ $(3.9 \pm 0{\cdot}1)^*$
4		West Bay (11)	$3{\cdot}1_3 \pm 0{\cdot}1_1$
5	39°47′N	139°18′E (#31)	$5{\cdot}4_8 \pm 0{\cdot}2_7$
6	42°35′N	135°29′E (#33)	$3{\cdot}8_7 \pm 0{\cdot}2_4$
7	40°27′N	135°47′E (#37)	$2{\cdot}2_1 \pm 0{\cdot}1_7$
8	36°51′N	132°18′E (#39)	$4{\cdot}4 \pm 0{\cdot}2_1$
9	38°35′N	131°00′E (#43)	$1{\cdot}7_8 \pm 0{\cdot}1_5$ $1{\cdot}9_8 \pm 0{\cdot}2_0$
10	30°40′N	130°44′E (#49)	$2{\cdot}8_8 \pm 0{\cdot}1_8$

Samples 5–10 were the top 20 mm of the cores.
* The value obtained by fusion of the sample with Na_2O_2, solvent extraction, *etc*, as in text.

Radiochemical analysis usually requires correction of the measured counting rate for the chemical recovery of the carrier added. In the present case, none of the ruthenium, either ^{106}Ru or carrier, was lost during the entire process, and the recovery of the carrier might always be taken as 100%. Therefore, determination of the chemical recovery can be omitted. Isotopic exchange between ^{106}Ru and the carrier is also no problem, because the results obtained by this method are fairly identical to those by the fusion method.

Confirmation of the separations, by neutron activation

When it is desired to determine the amounts of non-radioactive ruthenium and osmium in marine sediment, neutron-activation analysis will be preferred, since these amounts are too minute to be determined by spectrophotometry. In such a case CPA treatment of the irradiated sample may be accepted. The possibility of separation of active ruthenium and osmium from activated marine sediment was examined. A 0·5-g sample of marine sediment was loaded in a quartz ampoule and the end of the vessel was sealed. Reference standards of ruthenium and osmium were prepared by sealing a known amount of ruthenium chloride solution ($\sim 10^{-2}$ μg as Ru) and osmic acid solution ($\sim 10^{-2}$ μg as Os) in quartz ampoules, after evaporation to dryness with small portions of sodium hydroxide solution.[38] All these ampoules were put into another larger ampoule and the end of this was sealed. The ampoule was wrapped in aluminium foil and put into an aluminium capsule which was then irradiated for 80 hr in the Research Reactor of Kyoto University with a thermal neutron flux of about 4×10^{11} n/mm^2/sec. After cooling for a week, the ampoules were taken out of the capsule. Each ampoule was broken and its contents put into the CPA reaction vessel together with non-radioactive carriers. The decomposition and distillation processes were applied as described for ruthenium. The typical γ-spectra of each fraction of distillate from the irradiated sample standards are shown in Figs. 4 and 5, respectively. From these spectra, the osmium fraction after the Ce(IV)–CPA treatment is seen to be contaminated with other radioactive nuclides, mainly with ^{75}Se, and the ruthenium fraction after the Cr(VI)–CPA treatment is contaminated with ^{77}As, ^{51}Cr and ^{82}Br.

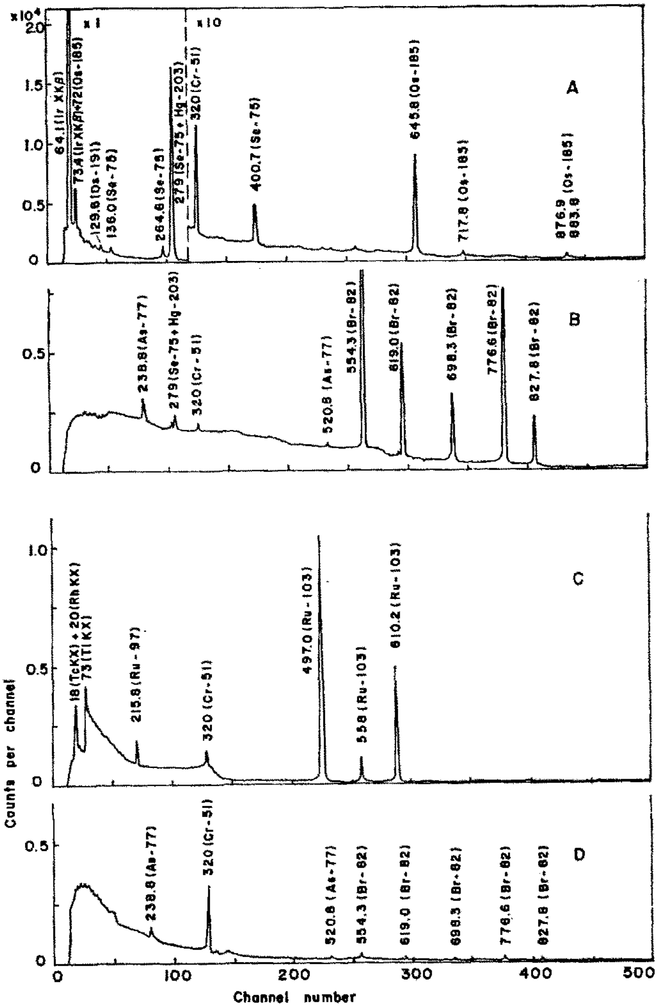


FIG. 4.—γ-Spectra of each fraction after the separation by CPA-method, obtained by Ge(Li) detector with 500-channel analyser.

Sample: irradiated marine sediment. (A) Os metal precipitated from Os-distillate. (B) Filtrate after (A). (C) Ru metal precipitated from Ru-fraction. (D) Filtrate after (C).

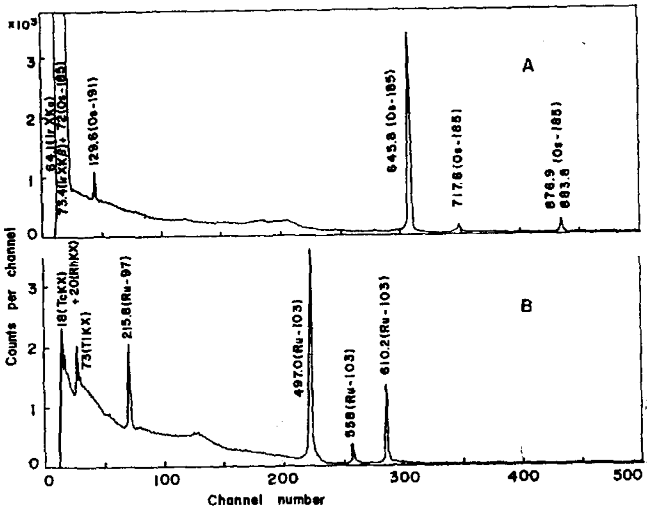


FIG. 5.—γ-Spectra of each reference standard of activated Ru and Os after being subjected to the Ce(IV)–CPA and Cr(VI)–CPA treatments, respectively.

The main radioactive nuclide generated after the neutron activation of marine sediment is ^{82}Br which shows its γ-ray spectrum especially in the osmium fraction after Ce(IV)–CPA treatment of the sample. Although some contaminating nuclides were distilled when metallic ruthenium was precipitated for radioactivity counting most of them passed into the filtrate, as shown in Figs. 4 and 5. The radioactive ruthenium consists of that from the ruthenium initially present in the marine sediment and that produced by fission of uranium in the sample. The spectra presented here refer to the separation of ruthenium from the marine sediment, not the determination of ruthenium present in the sample. In the osmium fraction, selenium and mercury are apt to be co-distilled, and they should be removed when this method is to be used for the activation determination of osmium. The activation determination of ruthenium and osmium by the use of this CPA treatment and some improved techniques[39] will be described elsewhere. However, it can be said now that this CPA method is specific for ruthenium and osmium in the separation of noble metals and more useful than other methods such as distilled from an aqueous solution.[40,41]

Acknowledgement—We are grateful to the members of the Research Reactor Institute of Kyoto University for their help with the activation of the samples and the radiochemical treatment.

Zusammenfassung—Ruthenium kann in verschiedenen chemischen Formen als Tetroxid aus unlöslichem Grundmaterial ausgetrieben werden. Man erhitzt dazu die Probe mit einem Reagens aus Chrom(VI) und kondensierter Phosphorsäure (abgekürzt als Cr(VI)-CPA). Wegen ihrer ausgezeichneten Zersetzungsfähigkeit für verschiedene feste Proben ist kondensierte Phosphorsäure sehr nützlich bei der chemischen Analyse verschiedener unlöslicher Materialien; gibt man ein Oxidationsmittel wie Kaliumdichromat zu dem CPA-Medium, dann tritt beim Erhitzen drastische Oxidation ein. Dieses Verfahren wird jetzt auf die Abtrennung von Ruthenium aus marinen Ablagerungen ausgedehnt. Während der Reaktion mit Cr(VI)-CPA wird Rutheniumtetroxid entwickelt und in einer Absorptionslösung aus 6*M* Salzsäure und Äthanol (1:1) gesammelt; Ruthenium wird dann spektrophotometrisch mit Thioharnstoff oder radiometrisch durch Zählen der β- oder, γ-Aktivität bestimmt. Osmium, das auf dieselbe Weise als

Tetroxid verflüchtigt werden kann, wird vorab durch Erhitzen der Probe mit Ce(IV)-CPA beseitigt; dieses Reagens entfernt Osmium, nicht aber Ruthenium. Die aufeinander folgenden Destillationen mit Ce(IV)-CPA und Cr(VI)-CPA geben zufriedenstellende Ergebnisse für die Trennung von Osmium und Ruthenium. Dieses Verfahren könnte sich zur Abtrennung von Ruthenium bei geochemischen oder Neutronenaktivierungsanalysen als nützlich erweisen.

Résumé—Le ruthénium sous des formes chimiques diverses peut être dégagé à l'état de tétroxyde de matières de matrice insolubles par chauffage de l'échantillon avec le réactif chrome(VI)-acide phosphorique condensé [en abrégé Cr(VI)-CPA]. En raison de son excellent pouvoir décomposant pour divers échantillons solides, l'acide phosphorique condensé est très utile dans l'analyse chimique de diverses matières insolubles, et lorsqu'un agent oxydant tel que le bichromate de potassium est ajouté au milieu CPA, une oxydation énergique se développe par chauffage. Cette méthode est maintenant étendue à la séparation du ruthénium des sédiments marins. Pendant la réaction avec Cr(VI)-CPA, le tétroxyde de ruthénium se dégage et est recueilli dans une solution d'aborption, mélange 1:1 d'acide chlorhydrique 6*M* et d'éthanol, et l'on dose alors le ruthénium spectrophotométriquement par la thiourée ou radiométriquement par comptage de l'activité β ou γ. L'osmium, qui peut être dégagé à l'état de tétroxyde par le même traitement, peut être éliminé auparavant par chauffage de l'échantillon avec Ce(IV)-CPA, qui élimine l'osmium, mais non le ruthénium. Les distillations successives au moyen de Ce(IV)-CPA et Cr(VI)-CPA donnent des résultats satisfaisants pour la séparation de l'osmium et du ruthénium. Cette méthode peut être utile pour la séparation du ruthénium en analyse géochimique ou par activation de neutrons.

REFERENCES

1. T. Kiba, *Kagaku to Kogyo*, 1958, **11**, 730; *Bunseki Kagaku*, 1960, **9**, 651.
2. S. Ohashi and H. Sugatani, *Bull. Chem. Soc. Japan*, 1957, **30**, 864.
3. Y. Umezaki, *Rept. Resources Res. Inst. Japan Govt.*, 1956, No. 36.
4. P. A. Avy, *Memor. Services Chimiq. de l'Etat*, 1955, 347.
5. Y. Yamazaki, *Bunseki Kagaku*, 1970 **19**, 187.
6. T. Kiba, T. Takagi, Y. Yoshimura and I. Kishi, *Bull. Chem. Soc. Japan*, 1955, **28**, 641.
7. T. Kiba, S. Ohashi, T. Takagi and Y. Hirose, *Bunseki Kagaku*, 1953, **2**, 448.
8. T. Takagi, *ibid.*, 1959, **4**, 625.
9. M. Ura, *Nippon Kagaku Zasshi*, 1957, **78**, 316.
10. F. D. Poppe and W. E. McEven, *Chem. Revs.*, 1958, **58**, 321.
11. M. Shinagawa, T. Yanagi and M. Goto, *Bunseki Kagaku*, 1966, **15**, 149.
12. E. W. Bilinski, D. E. Dieball and T. P. Whaley, *Anal. Chem.*, 1966, **38**, 1403.
13. G. G. Rao *et al.*, *Talanta*, 1962, **9**, 75; 1963; **10**, 169, 295, 1023, 1251; 1964, **11**, 705, 825, 1031; 1965, **12**, 953.
14. K. Motojima and A. Hoshino, *J. At. Energy Soc. Japan*, 1960, **2**, 1.
15. H. Onishi, N. Ishiwatari and H. Nagai, *Bull. Chem. Soc. Japan*, 1960, **33**, 1686.
16. S. Ohashi, *ibid.*, 1955, **28**, 171.
17. *Idem*, *ibid.*, 1955, **28**, 177.
18. J. Machida and N. Sugishita, *Nippon Kagaku Zasshi*, 1958, **79**, 528.
19. S. Ohashi, *Bull. Chem. Soc. Japan*, 1955, **28**, 537.
20. S. Ohashi and H. Makishima, *ibid.*, 1956, **29**, 700.
21. T. Takagi and N. Hayashi, *Nippon Kagaku Zasshi*, 1957, **78**, 445.
22. T. Takagi and Y. Tsuchiya, *Forensic Medicine, Kanazawa*, 1956, **2**, 126, 134, 201.
23. T. Kiba and I. Akaza, *Nippon Kagaku Zasshi*, 1960, **81**, 449.
24. H. Suzuki and S. Kawamura, *Bunseki Kagaku*, 1958, **7**, 181.
25. T. Kiba, I. Akaza and N. Sugishita, *Bull. Chem. Soc. Japan*, 1957, **30**, 972.
26. S. Akabori and T. Fujiwara, *Bull. Soc. Chim. Biol.*, 1958, **40**, 1983.
27. K. Kitagawa and N. Shibata, *Bunseki Kagaku*, 1960, **9**, 597.
28. T. Takeuchi, M. Suzuki and K. Yamamoto, *ibid.*, 1962, **12**, 752.
29. H. Terada and M. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, 1958, **61**, 1301.

30. T. Kiba, I. Akaza and O. Kinoshita, *Bull. Chem. Soc. Japan*, 1960, **33**, 329.
31. T. Kiba, I. Akaza and H. Hachino, *ibid.*, 1959, **32**, 454.
32. E. B. Sandel, *Colorimetric Determination of Traces of Metals.* 3rd Ed., p. 72. Interscience, New York, 1959.
33. I. M. Kolthoff and E. P. Elving, Eds., *Treatise on Analytical Chemistry*, Part II, Vol. 8, p. 480. Interscience, New York, 1963.
34. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon, Oxford, 1969.
35. E. I. Wyatt and R. R. Rickard, *The Radiochemistry of Ruthenium*, NAS-NS, 1961, 3029.
36. G. G. Rao, *Talanta*, 1963, **10**, 1251
37. G. Charlot and B. Tremillon, *Chemical Reactions in Solvents and Melts*, Pergamon, Oxford, 1969.
38. K. S. Chung and F. E. Beamish, *Anal. Chim. Acta*, 1968, **43**, 357.
39. R. Gijbels, *Talanta*, 1971, **18**, 587.
40. J. Krtil, J. Mencl and V. Bulovic, *Radiochem. Radioanal. Letters*, 1971, **6**, 219.
41. I. P. Alimarin, V. P. Khvostova and V. I. Shlenskaya, *J. Anal. Chem.* (*U.S.S.R.*), 1970, **25**, 2167.

1972, Vol. 19, pp. 465 to 472. Pergamon Press. Printed in Northern Ireland

TRACE ANALYSIS BY FLAMELESS ATOMIC-ABSORPTION SPECTROMETRY

TSUGIO TAKEUCHI and MASAAKI YANAGISAWA
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Chikusa-ku, Nagoya, Japan

MASAMI SUZUKI
Department of Industrial Chemistry, Faculty of Engineering,
Mie University, Kamihama-cho, Tsu-shi, Mie-ken, Japan

(*Received* 7 *June* 1971. *Accepted* 14 *September* 1971)

Summary—The operating conditions of an atomic-absorption system based on flameless atomization have been investigated for trace analysis for Al, Cr, Cu, Fe, Mg and Mn. The sample solution on a tantalum strip was atomized by electrical heating in an inert atmosphere within an absorption chamber. This technique allows the use of small sample sizes and results in a higher sensitivity than that with the conventional flame technique. Some interference effects and applications were investigated.

THE FLAME TECHNIQUE is normally used for the production of atomic populations in atomic–absorption spectrometry, because the nebulizer–burner systems provide simple, rapid, and accurate means of introducing sample solutions into the flame. However, the flame has some disadvantages as an atomizer. The atomization within the flame is very inefficient and the elements which form refractory oxides are extremely difficult to atomize even with a nitrous oxide–acetylene flame. Furthermore, flames contain sufficient free radical concentrations to combine with many elements to produce stable compounds, resulting in a lower degree of atomization and giving an absorption background at certain wavelengths. The low efficiency of nebulizers also affects the sensitivity. For most commercially available pneumatic nebulizing units, only 5–15% of the solution uptake finally reaches the flame, and very few elements are completely atomized in the flame.

Therefore, some new methods of atomization have been developed to improve sensitivity. Gatehouse and Walsh[1] described the use of a hollow-cathode sputtering device for the direct atomization of solid samples. Goleb and Brody[2] used a similar technique, in which the sample solution was evaporated on the walls of a suitable cathode. This technique is, however, cumbersome and limited in application. Nelson and Kuebler[3] atomized the sample by flash heating from a capacitor discharge lamp wound round a silica chamber which contained quartz or graphite strips to locate the sample and was purged by an inert gas. L'vov[4] described the use of a graphite furnace which was heated by an a.c. current in an atmosphere of argon. This technique required only a few μl of solution and promised to have a higher sensitivity, of the order of 10^{-9}–10^{-7} g. Massmann[5] has used an electrically heated graphite cell, and reported some sensitivities below 10^{-12} g. West and Williams[6] devised an efficient carbon filament reservoir, the sample solution being placed on the filament and atomized by means of passing a current. These authors have determined 10^{-10} g of silver and magnesium in a few μl of solution. Dogena and Burgess[7] also described a similar system in which atomization took place in the pressure range in the range of

1–400 mbar. Welz and Wiedeking[8] used a graphite tube furnace in analysis of copper and other elements in serum.

These flameless atomization methods demonstrate that only a few μl of liquid sample are required and that detection limits may be reached which are well below those obtained by conventional flame atomization. The electrothermal heating device should be useful for trace analysis.

This paper describes the parameters required to optimize the atomic absorption of various elements in an electrothermal heating device for flameless atomization. Further application possibilities for trace analysis are also discussed.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash AA-1E emission and atomic-absorption spectrophotometer, with the nebulizer–burner system removed, was used. The radiation from a hollow-cathode lamp (Hitachi, Hamamatsu TV and Westinghouse) was electronically modulated at 60 Hz, and the output from an R106 photomultiplier tube was connected to a Yanagimoto recorder (1-sec full-scale deflection). The instrument settings were adjusted to give the optimum working conditions. The following resonance lines were used: magnesium 285·2 nm, manganese 279·5 nm, copper 324·8 nm, iron 248·3 nm, chromium 357·9 nm, and aluminium 309·3 nm.

Absorption chamber. The absorption chamber used in this work is shown in Fig. 1. It was made of Pyrex glass and optical-quality silica end-windows were sealed onto the sides of the chamber. The tantalum strip was mounted between two copper rods which were insulated from each other and from the cork by binding Teflon round them and inserting them into quartz tubes passing through the cork in the bottom of the absorption chamber. Taps were sealed on the top of the chamber to allow the passage of a stream of inert gas through the chamber. A stopper at the top of the chamber allowed sample solutions to be deposited in a depression in the strip. The chamber was placed on the optical bench so that the beam from the hollow-cathode lamp was focused midway above the strip and then refocused on the entrance slit of the monochromator. The strip could be of nickel, tungsten, tantalum or platinum, and was heated by passing an electric current from a low voltage

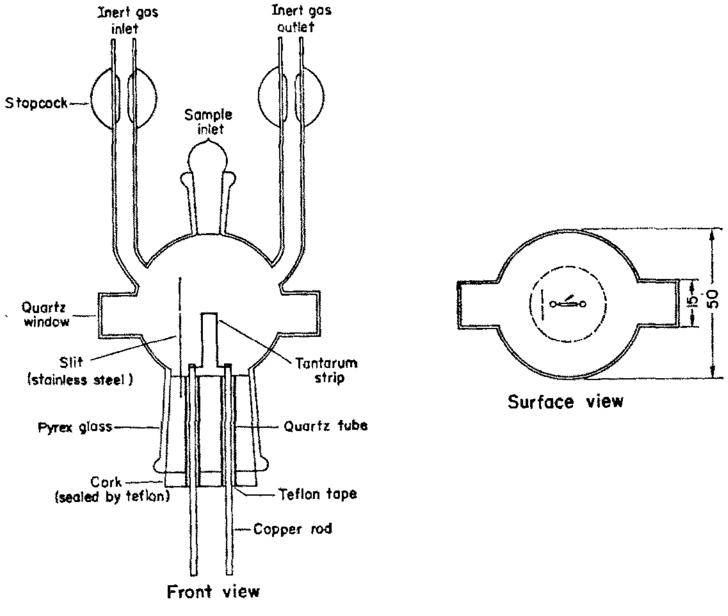


FIG. 1.—Atomization chamber.

transformer. The voltage was varied between 0 and 110 V with a maximum load current of 20 A. The temperature attained by the strip was measured with an optical pyrometer. The inert gas was supplied to the absorption chamber *via* a conventional flow-meter.

Procedure

The sample solution (2 μl) was placed in the depression in the strip with a Hamilton 10-μl microsyringe. The chamber was freed from air by flushing it with argon for 2 min. By passage of a low current through the strip in an atmosphere of inert gas, the solvent was evaporated without vaporization of the sample salts. The strip was then heated to vaporize and atomize the sample salts into the inert gas stream. All atomic-absorption signals were recorded and only peak signals were measured.

RESULTS AND DISCUSSION

Optimum analytical conditions

Strip material and voltage applied for atomization. The relationship between absorption signal and strip voltage is shown in Fig. 2. The absorption signal observed

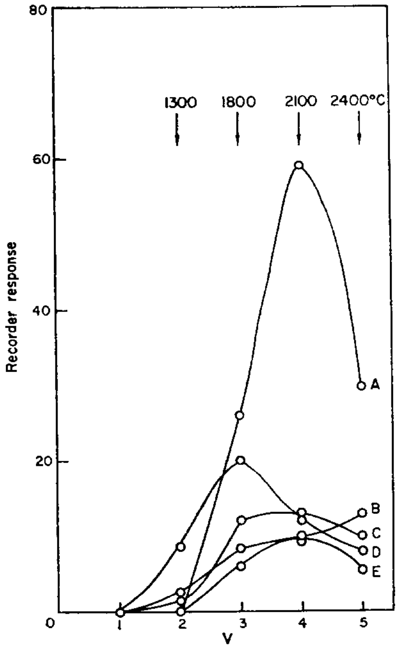


FIG. 2.—Effect of strip voltage (temperature) on atomic-absorption signal (chloride salts used).
A, 0·2 ng Mg; B, 0·6 ng Fe; C, 0·4 ng Mn;
D, 0·6 ng Cu; E, 0·8 ng Cr (flow-rate of argon: 3 l./min)

was transient, lasting a few seconds. The temperature attained by the strip is indicated in the figure. It can be seen that the optimum voltage differs for each element, and this may be due to a difference in the energy requirements for free atom production. The rate at which a sample was vaporized, and the atomization, were related to the temperature of the strip. Copper gave a narrower absorption signal than did magnesium, presumably because of the rapid atomization rate for copper; the width of the absorption signals for other elements was related to the atomization rates. Changing the temperature also broadened the signals. Increasing the voltage beyond the optimum value resulted in low peak signals owing to evaporation of the sample too quickly for monitoring by the amplifier. Although integration of the absorption signal might improve the sensitivity, the peak height was a reproducible measure of the concentration of the element.

Nickel, tungsten, tantalum and platinum were compared as strip material. Tantalum and tungsten showed similar results, but the tantalum strip was easier to fabricate. Only small signals were obtained with platinum, and neither nickel nor platinum could be used at very high temperature, so tantalum was chosen as the strip material. A continuous emission was observed, particularly in the wavelength range above 400 nm when the tantalum strip alone was heated, owing to light from the glowing strip entering the monochromater. Therefore, high precision was not obtained for elements having resonance lines in the longer wavelength range, because of the background.

Attempts were made to cover the strip with a small quartz tube, through which the beam from the hollow-cathode lamp passed. The sensitivity was improved, while the reproducibility was reduced because of the difficulty in accurate positioning of the strip in the tube.

Effect of inert gases and their flow-rate. An inert atmosphere is necessary within the absorption unit to prevent oxidation of the sample. Helium, argon and nitrogen were compared as inert gases, and reproducible results were obtained for a flowing system at atmospheric pressure as reported earlier.[6] The atomic-absorption signals were found to be unchanged for low concentrations of copper when different inert gases were used (Fig. 3). However, helium and nitrogen had a somewhat larger cooling effect upon the strip, as would be predicted from their thermal properties.

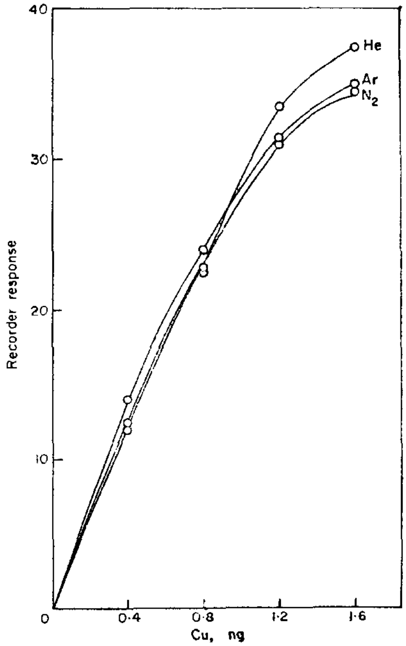


FIG. 3.—Effect of different inert gases (flow-rate of inert gas: ~2 l./min). Chlorides were used.

The temperature of the strip in nitrogen and helium was 8 and 16% lower, respectively, than that in argon at the same applied voltage. The cooling effect had little effect on the absorption signal, in contrast to the effect of strip temperature. No explanation can be found for this. As shown in Fig. 4, the magnesium absorption changed with increase in the flow-rate of argon. High inert gas flow-rates may have an adverse cooling effect on the atomic vapour. The argon flow-rate had different effects on measurement of other elements. The iron absorption was decreased with increasing flow rate whereas the chromium absorption was increased.

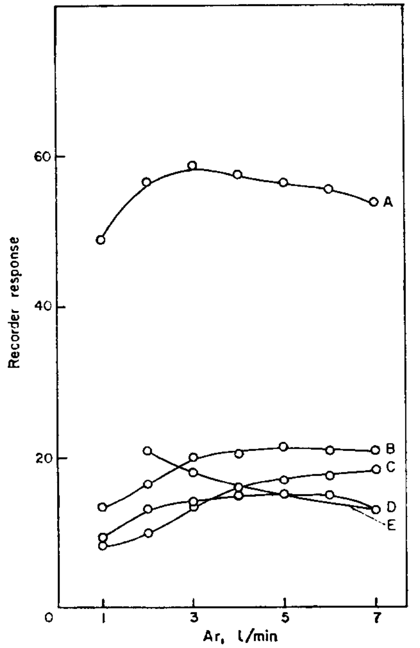


FIG. 4.—Effect of argon flow-rate on atomic-absorption signal.
A, 0·2 ng Mg; B, 0·6 ng Cu; C, 1·0 ng Cr;
D, 0·4 ng Mn; E, 1·0 ng Fe (used as chlorides)

The largest absorption signals were obtained when the light beam passed immediately above the strip.

Effect of the chemical composition of the sample. The chemical composition of the sample is important because thermal decomposition followed by atomization takes place before absorption. The nitrates and chlorides exhibited identical responses for copper, manganese and magnesium, while higher responses were obtained for chromium in the form of chromic salts than as chromate.

Reproducibility

The reproducibility of the method was determined by repetitively measuring standard solutions under optimized conditions, and calculating the coefficient of variation for each set of data. The coefficient of variation was 3–5% for all elements except iron (~7%). The volume delivered by the microsyringe had a coefficient of variation of 3%, so the main source of error was probably in delivery of the sample solution. Preheating of the strip was necessary before each analysis to remove any unwanted contamination on its surface.

Sensitivity

The absorption was plotted against the weight for each of the elements under conditions for maximum sensitivity. The curves obtained are shown in Fig. 5. The sensitivities (concentration which gives 1% absorption) were then calculated and are shown in Table I. The calibration curves showed increasing curvature at higher temperatures.

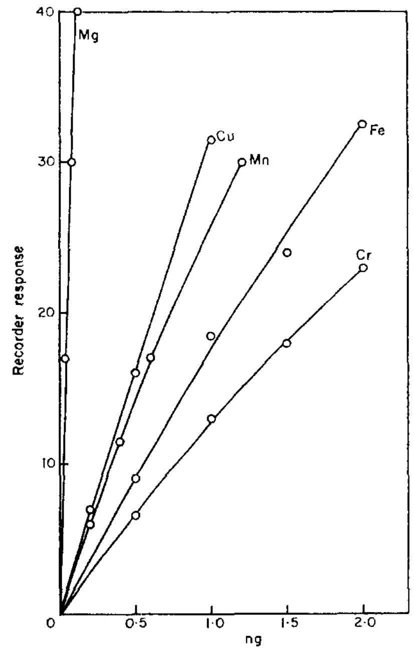


FIG. 5.—Calibration curves for magnesium, copper, manganese, iron and chromium (used as chlorides).

TABLE I.—SENSITIVITY

Element	Sensitivity, *g*
Mg (285·2 nm)	$3{\cdot}0 \times 10^{-12}$
Mn (279·5 nm)	$1{\cdot}0 \times 10^{-11}$
Cu (324·8 nm)	$1{\cdot}4 \times 10^{-11}$
Fe (248·3 nm)	$2{\cdot}0 \times 10^{-11}$
Cr (357·9 nm)	$3{\cdot}6 \times 10^{-11}$
Al (309·3 nm)	$6{\cdot}0 \times 10^{-11}$

Interferences

Interferences from aluminium and phosphate are encountered in the determination of magnesium, using a conventional flame. By the present technique, no such interferences were observed for [interferent]/[Mg] ratios up to 10. Higher concentrations of phosphate depressed the magnesium absorption. The interference due to aluminium depended on the magnesium concentration and the temperature as shown in Fig. 6. The presence of copper did not affect the magnesium absorption, but the absorption due to copper was affected by the presence of magnesium. No coherent theory can

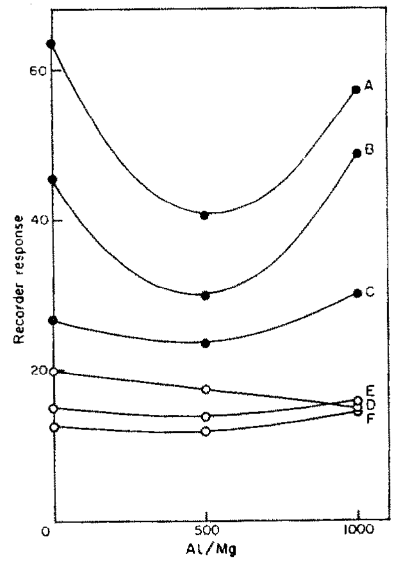


FIG. 6.—Interferences of aluminium in magnesium absorption (chlorides used).
A, 0·15 ng Mg(2100°); B, 0·10 ng Mg(2100°);
C, 0·05 ng Mg(2100°); D, 0·15 ng Mg(1800°);
E, 0·10 ng Mg(1800°); F, 0·05 ng Mg(1800°).

be advanced to explain these interferences, and much more work is needed on this aspect.

Potassium iodide (7 *μg*) was vaporized to examine molecular absorption in the wavelength region between 217·0 and 553·5 nm. Molecular absorption was observed at lower temperatures (1000°) as described previously by L'vov. Molecular absorption was not observed at higher temperatures (~2100°).

Applications

The value of the method was tested by selecting specific analytical applications. The magnesium concentration of control serum was measured by diluting 400-fold with water, and atomizing aliquots of the sample solution (2 *μl*) in the absorption device. Calibration was accomplished with known amounts of magnesium. The results are presented in Table II together with the certificate values.

TABLE II.—DETERMINATION OF MAGNESIUM IN SERUM

Sample	Mg found, *μg/ml*	Certificate value, *μg/ml*
A	24	23
B	59	61
C	25	21
D	34	31

A: Moni-Trol I (DADE Division, American Hospital Supply Corp., Miami, Fla.).

B: Moni-Trol II.

C: Versatol (General Diagnostics Division, Warner-Chilcott Lab., Morris Plain, N.J.).

D: Chemitrol (Clinton Lab., Los Angeles, Calif.).

An aluminium alloy (BCS 216/1) was also analysed for magnesium. With triplicate analyses, the values of 0·77, 0·80 and 0·78% were obtained. Calibration was accomplished using pure magnesium. These values were somewhat higher than the certified value of 0·74% (probably owing to interference by the aluminium). In this case the accuracy would be expected to be improved by the addition of aluminium to the standards. The standard addition method gave a value of 0·76% for magnesium.

This technique would appear to have considerable advantages in trace analysis where sample size is a limitation. Moreover, a solvent extraction method followed by atomization from the thermal strip could be suitable for determining trace amounts without a matrix effect.

Zusammenfassung—Die Arbeitsbedingungen eines Atomabsorptionssystems, das auf flammenloser Atomerzeugung beruht, wurden im Hinblick auf die Spurenanalyse nach Al, Cr, Cu, Fe, Mg und Mn untersucht. Die Probenlösung wurde auf einen Tantalstreifen aufgetragen und durch elektrische Heizung in inerter Atmosphäre in einer Absorptionskammer in den atomaren Zustand gebracht. Das Verfahren erlaubt geringe Probengrößen und erreicht eine höhere Empfindlichkeit als das herkömmliche Flammenverfahren. Einige Störeffekte und Anwendungen wurden untersucht.

Résumé—On a étudié les conditions de fonctionnement d'un système d'absorption atomique basé sur l'atomisation sans flamme pour l'analyse de traces de Al, Cr, Cu, Fe, Mg et Mn. La solution échantillon sur une lamelle de tantale est atomisée par chauffage électrique dans une atmosphère inerte à l'intérieur d'une chambre d'absorption. Cette technique permet l'emploi d'échantillons de petite dimension et conduit à une sensibilité plus grande que celle obtenue avec la technique de flamme ordinaire. On a étudié quelques effets d'interférences et applications.

REFERENCES

1. B. M. Gatehouse and A. Walsh, *Spectrochim. Acta*, 1960, **16**, 602.
2. J. A. Goleb and J. K. Brody, *Anal. Chim. Acta*, 1963, **28**, 457.
3. L. S. Nelson and N. A. Kuebler, *Proc. Xth Colloquim Spectroscop. Internationale*, 1963, p. 127.
4. B. V. L'vov, *Spectrochim. Acta*, 1969, **24B**, 53.
5. H. Massmann, *ibid.*, 1968, **23B**, 215.
6. T. S. West and X. K. Williams, *Anal. Chim. Acta*, 1969, **45**, 27.
7. H. M. Dogena and T. E. Burgess, *Anal. Chem.*, 1970, **42**, 1521.
8. B. Welz and E. Wiedeking, *Z. Anal. Chem.*, 1970, **252**, 111.

Talanta, 1972, Vol. 19, pp. 473 to 478. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM, URANIUM, THORIUM AND RARE EARTHS WITH ARSENAZO III AFTER EXTRACTIONS WITH THENOYLTRIFLUOROACETONE AND TRI-n-OCTYLAMINE*

HIROSHI ONISHI and KEIICHI SEKINE
Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan

(*Received* 7 *June* 1971. *Accepted* 7 *July* 1971)

Summary—A method is described for the spectrophotometric determination of microgram amounts of zirconium, uranium(VI), thorium and rare earths with Arsenazo III after systematic separation by extraction. First zirconium is extracted into a xylene solution of thenoyltrifluoroacetone (TTA) from about 4*M* hydrochloric acid. Uranium(VI) is then extracted into a xylene solution of tri-n-octylamine from about 4*M* hydrochloric acid. Thorium is next extracted into TTA solution at pH about 1·5, and finally rare earths are extracted into TTA solution at pH about 4·7. Each metal is back-extracted from the organic phase before determination.

ARSENAZO III (2,2′-[1,8-dihydroxy-3,6-disulpho-2,7-naphthylenebis(azo)]dibenzenearsonic acid) is an extremely sensitive colorimetric reagent for thorium, uranium, and zirconium and a sensitive one for rare earths.[1–3] Although microgram amounts of thorium and zirconium can be determined without separation,[4] determination of zirconium, uranium, thorium, and rare earths in their mixtures is difficult because of interference. Methods have been described for the separation of 5 μg of zirconium from 3 mg of thorium,[5] 20 μg of uranium from 10 mg of thorium or 10 mg of zirconium,[6,7] and for the separation of microgram amounts of thorium and uranium.[8] In each method, Arsenazo III has been used for determination.

The purpose of the present work is to develop a method for the systematic separation of zirconium, uranium, thorium, and rare earths and subsequent photometric determination with Arsenazo III. The separation method described herein will be generally useful.

EXPERIMENTAL

Reagents

Standard zirconium solution. A stock solution, containing 1·00 mg of zirconium/ml, was prepared by dissolving 3·533 g of $ZrOCl_2 \cdot 8H_2O$ in 2*M* hydrochloric acid, and diluting to exactly 1 litre with 2*M* hydrochloric acid. This solution was standardized by titration with EDTA, using Xylenol Orange as indicator.[9] A working standard solution was prepared by diluting the stock solution with 2*M* hydrochloric acid.

Standard uranium solution. A stock solution, containing 1·00 mg of uranium/ml, was prepared by dissolving 0·500 g of pure uranium metal in 10 ml of concentrated nitric acid and 12 ml of 30% hydrogen peroxide by heating. The solution was evaporated to near dryness. The residue was dissolved in 0·2*M* nitric acid and the solution was diluted to exactly 1 litre with 0·2*M* nitric acid. From this stock solution a working standard solution containing 10 μg of uranium/ml was prepared by diluting with water.

Standard thorium solution. A stock solution, containing 1·00 mg of thorium/ml, was prepared by dissolving 2·379 g of $Th(NO_3)_4 \cdot 4H_2O$ in 2*M* hydrochloric acid, and diluting to exactly 1 litre with

---

* Presented at the 19th Annual Meeting of the Japan Society for Analytical Chemistry, Nagoya, October, 1970.

2*M* hydrochloric acid. This solution was standardized by titration with EDTA, using Xylenol Orange as indicator.[9] A working standard solution was prepared by diluting the stock solution with 2*M* hydrochloric acid.

Stock solutions of lanthanum, dysprosium, and ytterbium. Each solution, containing 1·00 mg of metal/ml, was prepared by dissolving the previously ignited oxide in a slight excess of nitric acid (1 + 1) and diluting with water. Working standard solutions were prepared by diluting the stock solutions with water.

Standard cerium(III) *solution.* Water (10 ml), 70% perchloric acid (10 ml) and 30% hydrogen peroxide (1 ml) were added to 0·1228 g of previously ignited CeO_2. On heating, the oxide dissolved and the resulting solution was evaporated to dryness. Then 11 ml of sulphuric acid (1 + 1) and 1 ml of 30% hydrogen peroxide were added, and the solution was evaporated to white fumes. After cooling, the solution was diluted to exactly 100 ml with water. A working standard solution (10 μg of cerium/ml) was prepared by diluting this stock solution with water.

Thenoyltrifluoroacetone, 0·5*M*. TTA (45 g) was dissolved in 400 ml of xylene.

Tri-n-octylamine solution. TNOA (5 g) was dissolved in 100 ml of xylene.

Cresol Red solution. Cresol Red (100 mg) was dissolved in 26 ml of 0·01*M* sodium hydroxide and the solution was diluted to 250 ml with water.

Aqueous Arsenazo III solution, 0·10% *w/v*.

Procedure

An outline of the procedure is shown in Fig. 1.

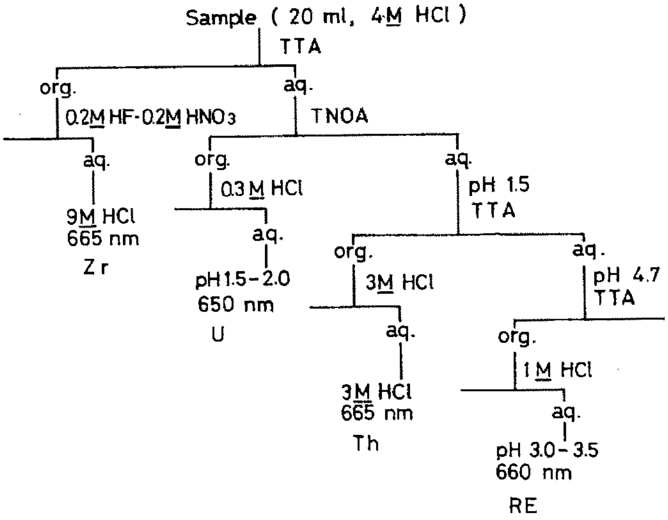


FIG. 1.—Outline of procedure.

Separation and determination of zirconium. Transfer the sample solution (4*M* in hydrochloric acid and containing 0–15 μg of zirconium, 0–50 μg of uranium, 0–30 μg of thorium, and 0–50 μg of a rare-earth element in a volume of approximately 20 ml) to a 100-ml separatory-funnel. Shake the solution for 10 min with 10 ml of TTA solution. When the layers have separated, drain off the aqueous phase into a second separatory-funnel. Wash the organic phase by shaking it for 5 min with 3 ml of 4*M* hydrochloric acid. Add this aqueous phase to the second separatory-funnel.

Add 10 ml of 0·2*M* hydrofluoric acid–0·2*M* nitric acid to the organic phase and shake for 3 min to back-extract the zirconium. Transfer the aqueous phase to a 50-ml quartz dish. Shake the organic phase for 30 sec with 3 ml of 0·2*M* hydrofluoric acid–0·2*M* nitric acid. Transfer the aqueous phase to the quartz dish and evaporate to dryness. (Discard the organic phase.) To the residue add 1 ml of concentrated nitric acid and 1 ml of 70% perchloric acid. Evaporate the solution to dryness, and dissolve the residue in 10 ml of concentrated hydrochloric acid.

Transfer the solution to a 25-ml volumetric flask, washing in with 8·5 ml of concentrated hydrochloric acid, add 1·0 ml of 0·1% Arsenazo III solution, and dilute to the mark with water. Measure the absorbance of the solution in a 1-cm cell at 665 nm, using the reagent blank as the reference.

Separation and determination of uranium. To the aqueous phase in the second separatory-funnel add 10 ml of TNOA solution and shake for 2 min. When the layers have separated, drain off the aqueous phase into a third separatory-funnel. Wash the organic phase by shaking it for 2 min with 3 ml of $4M$ hydrochloric acid. Add this aqueous phase to the third separatory-funnel.

Add 10 ml of $0{\cdot}3M$ hydrochloric acid to the organic phase and shake for 2 min to back-extract the uranium. Transfer the aqueous phase to a fourth separatory-funnel. Shake the organic phase for 1 min with 3 ml of $0{\cdot}3M$ hydrochloric acid. Add the aqueous phase to the fourth separatory-funnel. (Discard the organic phase.) Shake the aqueous phase containing uranium for 1 min with 5 ml of xylene.

Transfer the solution to a 25-ml volumetric flask through filter paper. Add 1 ml of 1% ascorbic acid solution [to reduce iron(III) if present], 1 drop of Cresol Red solution, dilute ammonia solution (1 + 9) until the colour turns to red from yellow (pH of the solution must be 1·5–2·0), 1·0 ml of Arsenazo III solution, and dilute to the mark with water. Measure the absorbance of the solution at 650 nm, using the reagent blank as the reference.

Separation and determination of thorium. To the aqueous phase in the third separatory-funnel add 1 drop of Cresol Red solution, concentrated ammonia solution until the colour of the aqueous phase turns to red from yellow (pH of the solution must be 1·5 – 2·0), and 10 ml of $0{\cdot}5M$ TTA, and shake the system for 15 min. When the layers have separated, drain off the aqueous phase into a fifth separatory-funnel.

Shake the organic phase for 10 min with 10 ml of $3M$ hydrochloric acid to back-extract the thorium. Transfer the aqueous phase to a sixth separatory-funnel. Shake the organic phase for 5 min with 5 ml of $3M$ hydrochloric acid. Add the aqueous phase to the sixth separatory-funnel. (Discard the organic phase.) Shake the combined aqueous phases for 1 min with 5 ml of xylene.

Transfer the aqueous solution to a 25-ml volumetric flask through filter paper. Wash the organic phase by shaking it for 30 sec with 5 ml of $3M$ hydrochloric acid. Transfer the aqueous solution to the same volumetric flask through the filter paper. Add 1 ml of concentrated hydrochloric acid and 1·0 ml of Arsenazo III solution and dilute to the mark with water. Measure the absorbance of the solution at 665 nm, using the reagent blank as the reference.

Separation and determination of a rare earth. To the aqueous phase in the fifth separatory-funnel, add 50% w/v ammonium acetate solution until the pH of the solution becomes 4·7 ± 0·2 (pH test paper) and 15 ml of $0{\cdot}5M$ TTA, and shake the system for 5 min. When the layers have separated, drain off the aqueous phase into a seventh separatory-funnel. Add 15 ml of TTA solution to the seventh separatory-funnel, and shake the system for 5 min. Discard the aqueous phase. Combine the second extract with the first and wash the extracts by equilibrating them for 1 min with 10 ml of $0{\cdot}1M$ acetate buffer solution of pH 4·7. Discard the aqueous phase.

Shake the organic phase for 5 min with 25 ml of $1M$ hydrochloric acid to back-extract the rare earth. Transfer the aqueous phase to a 50-ml quartz dish and evaporate to dryness. To the residue add 1 ml of concentrated nitric acid and 1 ml of 70% perchloric acid. Evaporate the solution to dryness.

Dissolve the residue in 15 ml of water and transfer the solution to a 25-ml volumetric flask. Add 1 ml of 50% ammonium acetate solution and $4M$ hydrochloric acid until the pH of the solution becomes 3·0–3·5 (pH test paper). Add 1·0 ml of Arsenazo III solution and dilute to the mark with water. Measure the absorbance of the solution at 660 nm, using the reagent blank as the reference.

Calibration curves. Construct calibration curves for zirconium (0–15 μg), uranium (0–50 μg), thorium (0–30 μg), and rare earth (0–50 μg) by omitting the separation steps.

RESULTS AND DISCUSSION

Determination of zirconium, uranium, thorium, and rare earths

The conditions for the spectrophotometric determination of zirconium,[4] uranium,[7] and thorium[4] have been already described. The addition of gelatin in the determination of zirconium[4] has been found unnecessary. Although uranium can be determined more sensitively by making use of the uranium(IV)–Arsenazo III complex,[6,10] the present work is based on the uranium(VI)–Arsenazo III complex,[7,10] because of simpler manipulation. In the present work, molar absorptivities of $12{\cdot}9 \times 10^3$, $4{\cdot}4 \times 10^3$, and $10{\cdot}2 \times 10^3$ $\mathrm{l.mole^{-1}.mm^{-1}}$ have been obtained for zirconium, uranium, and thorium, respectively.

The conditions for the determination of rare earths (dysprosium has been chosen to represent rare earths) have been examined. The absorption curves are shown in Fig. 2. A wavelength of 660 nm has been adopted for the determination of rare earths.

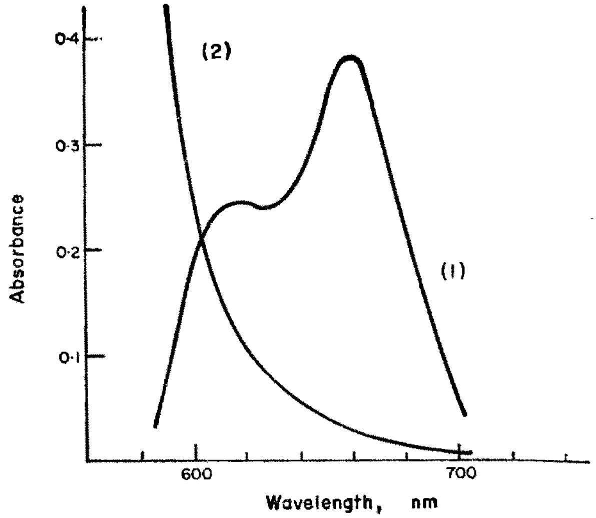


FIG. 2.—Absorption curves at pH 3·0.
(1) Dy (40 μg/25 ml) and Arsenazo III (1 mg/25 ml) *vs.* reagent blank.
(2) Reagent blank *vs.* water.

The effect of pH on the absorbance of the dysprosium–Arsenazo III complex is shown in Fig. 3. A suitable pH range is 3·0–3·5. The molar absorptivities at 660 nm are $4{\cdot}1 \times 10^3$, $4{\cdot}0 \times 10^3$, $4{\cdot}2 \times 10^3$, and $3{\cdot}4 \times 10^3$ $\text{l.mole}^{-1}.\text{mm}^{-1}$ for La, Ce, Dy, and Yb, respectively. These values are a little lower than those given by Savvin.[3]

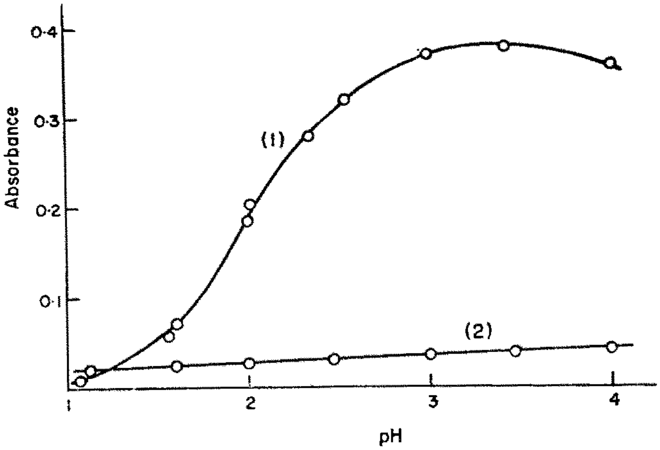


FIG. 3.—Effect of pH on absorbance at 660 nm.
(1) Dy (40 μg/25 ml) and Arsenazo III (1 mg/25 ml) *vs.* reagent blank.
(2) Reagent blank *vs.* water.

Separation of zirconium, uranium, thorium, and rare earths

The conditions for the separation of zirconium from thorium,[5] uranium from thorium,[6,7] and thorium and uranium[8] have been already clarified. Separation of rare earths by TTA extraction was previously studied.[11] On the basis of these investigations a scheme has been evolved for the analysis of mixtures of zirconium, uranium, thorium, and rare earths (Fig. 1).

TABLE I.—DETERMINATION OF Zr, U, Th, AND RARE EARTHS

Taken, *μg*				Found, *μg*			
Zr	U	Th	Dy	Zr	U	Th	Dy
10·1	0	0	0	9·9, 9·9	0, 0	0, 0	0, 0
0	30·0	0	0	0, 0	$27{\cdot}_0$, $27{\cdot}_0$	0, 0	0, 0
0	0	19·3	0	0, 0	0, 0	$18{\cdot}_4$, $18{\cdot}_6$	0, 0
0	0	0	30·0	0, 0	0, 0	0, 0	$29{\cdot}_1$, $29{\cdot}_1$
15·2	30·0	19·3	0	$13{\cdot}_9$, $13{\cdot}_7$	$27{\cdot}_0$, $27{\cdot}_0$	$18{\cdot}_8$, $18{\cdot}_8$	0, 0
0	50·0	19·3	10·0	0, 0	$45{\cdot}_5$, $45{\cdot}_5$	$18{\cdot}_5$, $19{\cdot}_2$	9·5, 9·7
5·1	0	29·0	30·0	5·1, 5·1	0, 0	$27{\cdot}_1$, $27{\cdot}_1$	$29{\cdot}_6$, $30{\cdot}_0$
10·1	30·0	0	50·0	9·9, 9·9	$26{\cdot}_5$, $27{\cdot}_0$	0, 0	$49{\cdot}_0$, $49{\cdot}_0$
10·1	30·0	19·3	30·0	9·9, 9·6	$26{\cdot}_5$, $26{\cdot}_5$	$18{\cdot}_4$, $18{\cdot}_8$	$28{\cdot}_5$, $28{\cdot}_5$
10·1	30·0	19·3	30·0	9·4, 9·2	$27{\cdot}_0$, $26{\cdot}_5$	$18{\cdot}_8$, $18{\cdot}_8$	$28{\cdot}_8$, $28{\cdot}_9$
10·1	30·0	19·3	30·0*	9·5, 9·5	$27{\cdot}_0$, $27{\cdot}_5$	$17{\cdot}_9$, $18{\cdot}_0$	$29{\cdot}_3$,* $29{\cdot}_8$*

* La instead of Dy.

Results obtained in applying the proposed procedure are collected in Table I. Recoveries of uranium are a little low (~ 90%). After extraction of uranium with TNOA solution, the organic phase was diluted with an equal volume of xylene, and uranium was back-extracted with 0·3*M* hydrochloric acid. The recovery of uranium was not improved by this procedure.

Occasionally high blank values for zirconium were obtained. This was due to traces of zirconium in the glass of the separatory-funnels. Separatory-funnels can be found which do not yield appreciable amounts of zirconium on treatment with 0·2*M* hydrofluoric acid–0·2*M* nitric acid. However, if such separatory-funnels are not available, plastic separatory-funnels may be necessary for the back-extraction step.

TABLE II.—EFFECT OF FOREIGN IONS

Additions			Found, *μg*			
			Zr	U	Th	Dy
Fe(III)	1 mg	Zr 10·1 *μg* U 30·0 *μg* Th 19·3 *μg* Dy 30·0 *μg*	9·6, 9·7	$27{\cdot}_5$, $27{\cdot}_5$	$18{\cdot}_4$, $18{\cdot}_4$	$28{\cdot}_5$, $28{\cdot}_9$
SO_4^{2-}	1 mmole	Zr 10·1 *μg* U 30·0 *μg* Th 19·3 *μg* Dy 30·0 *μg*	9·3, 9·6	$27{\cdot}_2$, $27{\cdot}_0$	$18{\cdot}_4$, $18{\cdot}_5$	$29{\cdot}_0$, $29{\cdot}_7$
PO_4^{3-}	1 mmole	Zr 10·1 *μg* U 30·0 *μg* Th 19·3 *μg* Dy 30·0 *μg*	2·9, 4·0	$26{\cdot}_5$, $27{\cdot}_5$	5·8, 5·0	$22{\cdot}_4$
PO_4^{3-}	0·05 mmole	Zr 10·1 *μg* U 30·0 *μg* Th 19·3 *μg* Dy 30·0 *μg*	9·7, 9·7	$27{\cdot}_0$, $27{\cdot}_0$	$13{\cdot}_1$, $14{\cdot}_2$	$28{\cdot}_0$, $29{\cdot}_0$
PO_4^{3-}	0·01 mmole	Th 19·3 *μg* Dy 30·0 *μg*	Not detd.*	Not detd.*	$18{\cdot}_1$, $18{\cdot}_3$	$28{\cdot}_4$, $28{\cdot}_3$
Sc	50 *μg*	Zr 0 *μg* U 0 *μg* Th 0 *μg* Dy 0 *μg*	0, 0	0, 0	0, 0	0, 0

* Not determined.

Smaller amounts of uranium may be determined if uranium(VI) is reduced to uranium(IV) with zinc and then the colour is developed with Arsenazo III in hydrochloric acid solution.[6]

As shown in Table I, the recovery of lanthanum is the same as that of dysprosium. It is believed that other rare-earth elements will give similar results.[11]

Interference study. The effect of selected foreign ions on the separation and determination of zirconium, uranium, thorium, and dysprosium is shown in Table II. Although scandium will accompany thorium in the separation step,[12] it does not interfere with the determination of thorium. One mmole of phosphate does not interfere with the analysis for uranium, but it does with the analysis for the other elements; 0·05 mmole of phosphate still interferes with the analysis for thorium, but 0·01 mmole of phosphate does not.

Zusammenfassung—Es wird ein Verfahren zur spektrophotometrischen Unter scheidung von Mikrogrammengen von Zirkonium, Uran(VI), Thorium und seltenen Erden mit Arsenazo III nach systematischer Trennung durch Ausscheidung beschrieben. Zuerst wird Zirkonium in eine Xylollösung von Thenoyltrifluoroaceton (TTA) aus etwa 4M Chlorhydratsäure ausgeschieden. Dann wird Uran(VI) in eine Xylollösung von Tri-n-oktylamin aus etwa 4*M* Chlorhydratsäure ausgeschieden. Danach wird Thorium in eine TTA Lösung bei etwa pH 1,5 und zum Schluss seltene Erden in eine TTA Lösung bei etwa pH 4,7 ausgeschieden. Jedes Metall wird vor Unterscheidung von der organischen Phase zurück titriert.

Résumé—On décrit une méthode pour la détermination spectrophotométrique de quantités de l'ordre du microgramme de zirconium, uranium(VI), thorium et terres rares avec l'Arsenazo III après séparation systématique par extraction. On extrait d'abord le zirconium de l'acide chlorhydrique environ 4*M* dans une solution en xylène de thenoyltrifluoracétone (TTA). On extrait alors l'uranium(VI) de l'acide chlorhydrique environ 4*M* dans une solution en xylène de tri-*n*-octylamine. Le thorium est ensuite extrait par la solution de TTA à un pH d'environ 1,5 et, finalement, les terres rares sont extraites par la solution de TTA à un pH d'environ 4,7. Chaque métal est extrait en retour de la phase organique avant le dosage.

REFERENCES

1. S. B. Savvin, *Talanta*, 1961, **8**, 673.
2. *Idem*, *ibid.*, 1964, **11**, 1.
3. *Idem*, *Arsenazo III*, Atomizdat, Moscow, 1966.
4. H. Onishi, *Bunseki Kagaku*, 1963, **12**, 1153.
5. H. Onishi and Y. Toita, *ibid.*, 1964, **13**, 1271.
6. *Idem*, *ibid.*, 1965, **14**, 1141.
7. *Idem*, *ibid.*, 1969, **18**, 592.
8. H. Onishi and K. Sekine, *ibid.*, 1970, **19**, 547.
9. J. Körbl, R. Přibil and A. Emr, *Collection Czech. Chem. Commun.*, 1957, **22**, 961.
10. H. Onishi and K. Sekine, *Bunseki Kagaku*, 1969, **18**, 524.
11. H. Onishi and C. V. Banks, *Talanta*, 1963, **10**, 399.
12. *Idem*, *Anal. Chim. Acta*, 1963, **29**, 240.

Talanta, 1972, Vol. 19, pp. 479 to 487. Pergamon Press. Printed in Northern Ireland

FORMATION AND COMPOSITION OF THE PRECIPITATES OF VARIOUS METAL 8-SELENOQUINOLINE COMPLEXES

Eiichi Sekido, Isamu Fujiwara and Yoshitaka Masuda
Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan

(*Received* 19 *June* 1971. *Accepted* 1 *December* 1971)

Summary—The effect of acidity on the precipitation of various bivalent metal 8-selenoquinoline and 8-mercaptoquinoline complexes has been systematically studied and compared. The metal ions were Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+}. Most of the metal ions, except copper(II) and cobalt(II), precipitate as a 1:2 complex, metal:ligand. However, in hydrochloric acid solution cadmium precipitates as $CdR_2 \cdot 2HCl$ and lead as $PbR_2 \cdot 2HCl$ or $PbR \cdot Cl$. Copper(II) is reduced to copper(I) and precipitates as $CuR \cdot RH$ at pH above 2·0 and as CuR in strongly acidic solution. Cobalt(II) does not give a precipitate of composition but appears to precipitate as a mixture of $CoR_2 \cdot RH$ and fixed CoR_2 or as other complexes. The reasons for the formation of the various types of precipitate are considered.

From the viewpoint of selectivity of organic reagents it is particularly interesting to investigate the change of reactivity of 8-hydroxyquinoline with a metal ion when the donor oxygen atom is replaced by a sulphur or a selenium atom. The formation of 8-hydroxyquinoline precipitates with various metal ions was systematically studied by Goto,[1] and the various metal 8-mercaptoquinoline complexes were formed by Kuznetsov, Bamkovsky and Ievin'sh[2] for the first time. For 8-selenoquinoline, systematic studies have not been made although qualitative results for the formation of precipitates and their chloroform extraction were reported by Sekido, Fernando and Freiser.[3] The present paper is concerned with stoichiometric studies on the formation and composition of the precipitates of various bivalent metal 8-selenoquinoline complexes, and comparisons with those of 8-mercaptoquinoline and 8-hydroxyquinoline.

EXPERIMENTAL

Reagents

Sodium salts of 8-selenoquinoline and 8-mercaptoquinoline. 8-Selenoquinoline was synthesized by the modified method of Sekido, Fernando and Freiser,[4] and its sodium salt monohydrate was prepared by the method of Sekido and Fujiwara.[5] The sodium salt of 8-mercaptoquinoline anhydride was prepared by the method of Nakamura and Sekido.[6] Both of the reagent solutions were prepared as follows. An amount of 8-selenoquinoline corresponding to 50% excess over that required stoichiometrically for complete precipitation of a known quantity of metal ion was dissolved in a mixed solution of 2 ml of 50% hypophosphorous acid, 2 ml of 6*M* hydrochloric acid and 10 ml of water. 8-Mercaptoquinoline solution was prepared in the same manner but without hypophosphorous acid.

Buffer solutions. A 1*M* acetic acid–1*M* sodium acetate buffer was used for weakly acidic medium and 1*M* ammonia–1*M* ammonium chloride and Clark-Lubs buffer solution for weakly basic medium. Hydrochloric acid and sodium hydroxide solution were used for strongly acidic and basic media respectively.

Stock solutions of bivalent metal ions, 0·1*M*. Stock solutions of Zn^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+} and Co^{2+} were prepared by dissolving their salts in demineralized water. Their concentrations were determined with EDTA.

All reagents, including masking reagents, were of analytical-reagent grade.

Precipitation of the complexes

In order to find the effect of pH on the formation of the 8-selenoquinoline or 8-mercaptoquinoline complexes other conditions must be kept the same. Thus the conditions such as excess of reagent, temperature, aging time, use of reducing agents, washing and drying of the precipitates, were first examined.

The following procedures were adopted. Metal solution (0·1*M*, 10 ml) and 50 ml of water were taken in a 200-ml Erlenmeyer flask and adjusted to a definite pH with 20 ml of 1*M* buffer solution. If necessary, a masking reagent such as tartaric acid was added to prevent alkaline hydrolytic precipitation. The resulting solution was heated to 65–75° under nitrogen, and the reagent solution (50% excess) was added. After aging for about 10 min, the precipitate was collected and washed with 50 ml of hot solution at 80° adjusted approximately to the desired pH with hydrochloric acid or sodium hydroxide and then with 50 ml of hot water. All the operations were conducted under a blanket of nitrogen gas. The precipitate was dried to constant weight, in a desiccator charged with silica gel.

Determination of composition of the precipitates

About 0·1 g of the precipitate was weighed into a crucible and decomposed by heating with 18 ml of concentrated nitric acid and 6 ml of 60% perchloric acid. The procedure was repeated until the organic matter was completely destroyed. The resulting clear solution was titrated with 0·1*M* EDTA.

RESULTS AND DISCUSSION

The effect of acidity on the formation of the precipitates of the bivalent metal 8-selenoquinoline and 8-mercaptoquinoline complexes is shown in Figs. 1–6. The results for the formation of the precipitates are summarized in Table I. Most of the metal ions except for copper(II) and cobalt(II) precipitate stoichiometrically as the 1:2 complex, MR_2. However, in hydrochloric acid solution cadmium precipitates as $CdR_2 \cdot 2HCl$ and lead as $PbR_2 \cdot 2HCl$ or $PbR \cdot Cl$ for 8-selenoquinoline, and lead precipitates as $PbR \cdot Cl$ for 8-mercaptoquinoline. Copper(II) seems to precipitate as $CuR \cdot RH$ at pH > 2·0 and as CuR in strongly acidic solution. Cobalt(II) does not give precipitates of a definite composition, but appears to precipitate as a mixture of $CoR_2 \cdot RH$ and CoR_2 or as other complexes (*e.g.* CoR_3). The 8-seleno- and 8-mercaptoquinoline precipitates have no co-ordinated water although most of the bivalent metal 8-hydroxyquinoline complexes have two molecules of water of co-ordination.

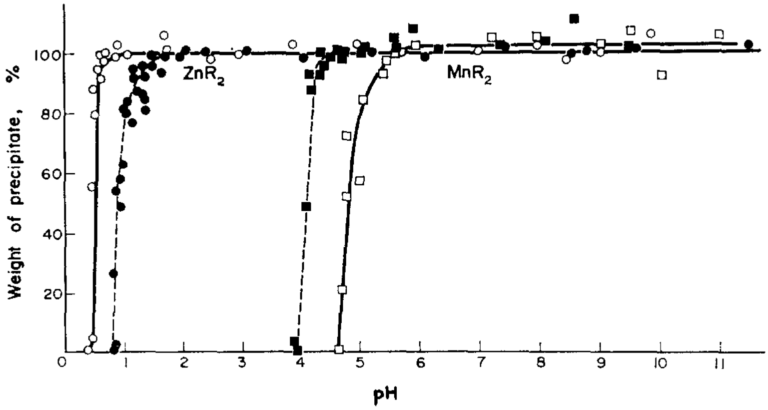


Fig. 1.—The effect of acidity on formation of zinc and manganese 8-selenoquinoline precipitates (———) and 8-mercaptoquinoline precipitates (– – – –). ○ and ●: zinc complexes; □ and ■: manganese complexes. The term "weight of precipitate (%)" *refers to the precipitate weight relative to the theoretical weight corresponding to the species indicated.*

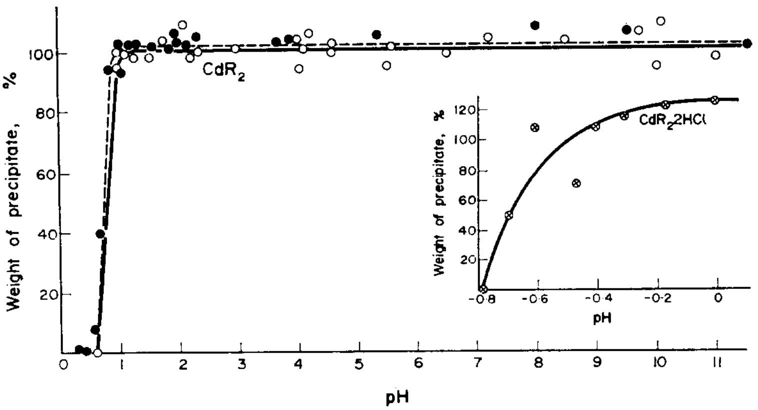


FIG. 2.—The effect of acidity on formation of cadmium 8-selenoquinoline (—○—) and cadmium 8-mercaptoquinoline (- -●- -) precipitates. ⊗ indicates precipitates formed on cooling or standing at low temperature.

The minimum pH for complete precipitation of the 1:2 metal complex increases in the order Zn < Cd < Ni < (Co) < Pb < (Cu) < Mn for 8-selenoquinoline complexes and Cd < Ni < (Co) < Zn < (Cu) < Pb < Mn for 8-mercaptoquinoline complexes. The values for cobalt and copper are those for $CoR_2 \cdot RH$ and $CuR \cdot RH$ respectively. In order to compare these orders qualitatively with that for 1:2 metal 8-hydroxyquinoline complexes, Goto's data[1] are cited below although the conditions of the formation of these precipitates is a little different from those used for this study.

Metal:	Cu	Ni	Zn	Co	Cd	Mn	Pb
pH:	2·7	4·0	4·1	4·2	5·4	5·9	8·4

On the basis of proton affinity, the pH of formation of the precipitate of the same metal would be expected to decrease in the order of the value of $pK_{a_1} + pK_{a_2}$ for the three reagents, 15·01 for 8-hydroxyquinoline,[7] 10·40 for 8-mercaptoquinoline[4] and 8·67 for 8-selenoquinoline.[4] This relation seems to hold between the 8-hydroxyquinoline complex and either of the other two reagent complexes but not between the

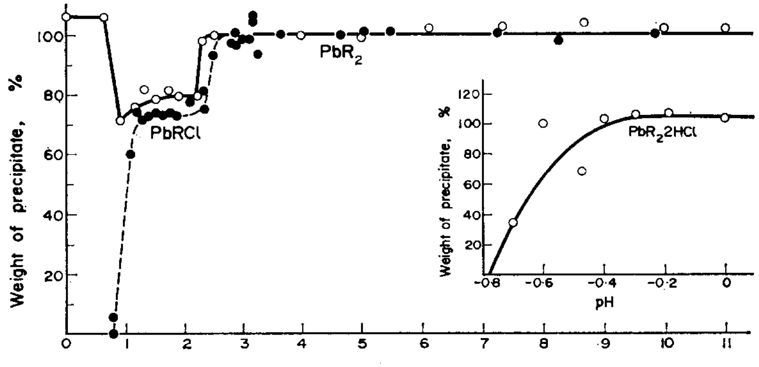


FIG. 3.—The effect of acidity on formation of lead 8-selenoquinoline (—○—) and lead 8-mercaptoquinoline (- -●- -) precipitates.

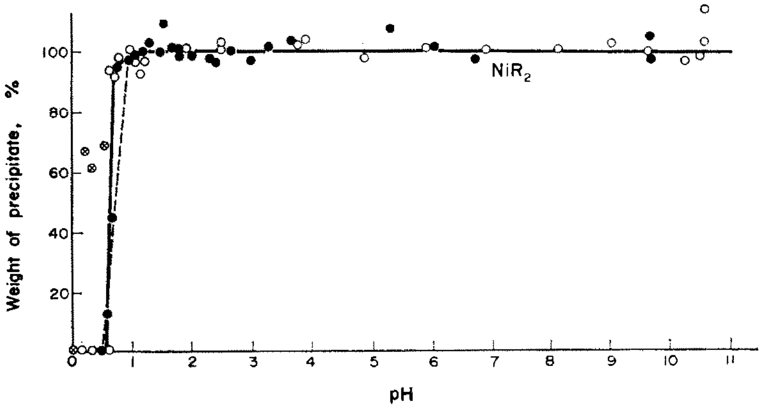


FIG. 4.—The effect of acidity on the formation of nickel 8-selenoquinoline (—○—) and nickel 8-mercaptoquinoline (– –●– –) precipitates. ⊗ indicates nickel 8-selenoquinolinate formed on standing at low temperature.

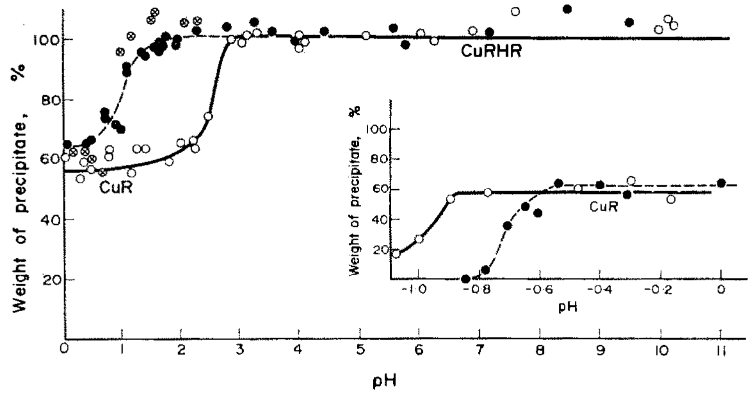


FIG. 5.—The effect of acidity on the formation of copper 8-selenoquinoline (—○—) and copper 8-mercaptoquinoline (– –●– –) precipitates. ⊗ indicates copper 8-selenoquinoline complex formed without hypophosphorous acid present.

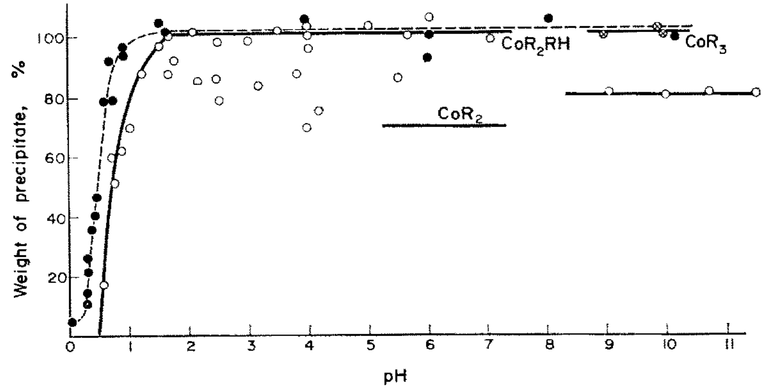


FIG. 6.—The effect of acidity on the formation of cobalt 8-selenoquinoline (—○—) and cobalt 8-mercaptoquinoline (– –●– –) precipitates. ⊗ indicates the precipitate of cobalt 8-selenoquinolinate formed from $Co(NH_3)_6^{3+}$.

TABLE I.—FORMATION OF PRECIPITATES FOR VARIOUS METAL 8-SELENO AND 8-MERCAPTOQUINOLINE COMPLEXES

Metal	pH at which pptn. begins	pH at which complete pptn. begins	Elemental analysis, % C		H		N		Mole ratio		Composition of precipitate	Colour of the precipitate
			Found	Calcd.	Found	Calcd.	Found	Calcd.	Metal	Ligand		
						8-Selenoquinoline complexes						
Zn	0·45	0·75	44·9	45·08	2·5	2·52	6·1	5·84	1	2·0	ZnR_2†	Yellow
									1	2·0	ZnR_2	Orange*
Cd	0·60	1·05	40·7	41·05	2·2	2·30	5·5	5·32	1	2·0	CdR_2	Yellow orange
	−0·75	0·60									$CdR_2{\cdot}2HCl$	Red orange
Pb	2·25	2·55	34·9	34·79	2·2	1·95	4·5	4·51	1	2·0	PbR_2	Dull yellow
	0·90	2·20									PbRCl	Gray green
	−0·75	0·70									$PbR_2{\cdot}2HCl$	Red orange
Mn	4·64	5·90	46·0	46·29	2·6	2·58	6·3	5·97	1	2·2	MnR_2	Gray brown
			45·6		3·0		6·1		1	2·1	MnR_2	Dark brown*
Ni	0·60	1·10	46·0	45·71	2·7	2·56	5·0	5·92	1	2·0	NiR_2	Violet black
	0·00	0·60									NiR_2	Violet black*
Cu	2·0	2·90	45·4	45·25	2·6	2·53	6·2	5·86	1	2·2	CuR·RH	Brown
	<−1·1	−0·89									CuR	Black
Co	0·55	1·66	47·7	47·60	2·8	2·81	6·5	6·17	1	3·1	$CoR_2{\cdot}RH$	Red brown
			44·4	45·69	3·1	2·56	5·9	5·92	1	2·3	CoR_2	Brown
			47·9	47·67	3·3	2·67	6·6	6·18			CoR_3‡	Light brown
						8-Mercaptoquinoline complexes						
Zn	0·75	1·50	56·1	56·04	3·2	3·14	7·4	7·26	1	2·0	ZnR_2	Yellow
									1	2·0	ZnR_2	Orange yellow*
Cd	0·60	1·00	49·6	49·95	2·6	2·80	6·5	6·47	1	2·0	CdR_2	Yellow orange
Pb	2·30	2·60	41·3	40·98	2·5	2·26	5·6	5·31	1	2·0	PbR	Yellow
	0·80	2·30							1	1·0	PbR_2Cl	Dull yellow
Mn	3·95	4·60	53·1	57·59	3·4	3·22	7·0	7·46	1	2·0	MnR_2	Yellow brown
Ni	0·50	1·15	57·4	57·02	3·5	3·19	7·4	7·39	1	2·0	NiR_2	Dark brown
Cu	0·55	2·10	56·2	56·31	3·4	3·15	7·4	7·29	1	2·0	CuR·RH	Yellow brown
	−0·79	0·55							1	1·0	CuR	Black
Co				59·99		3·54		7·77	1	3	$CoR_2{\cdot}RH$	Dark brown
	<0·0	1·25		56·94		3·19		7·38			CoR_2	

* At the lower pH at which the complex begin to precipitate.

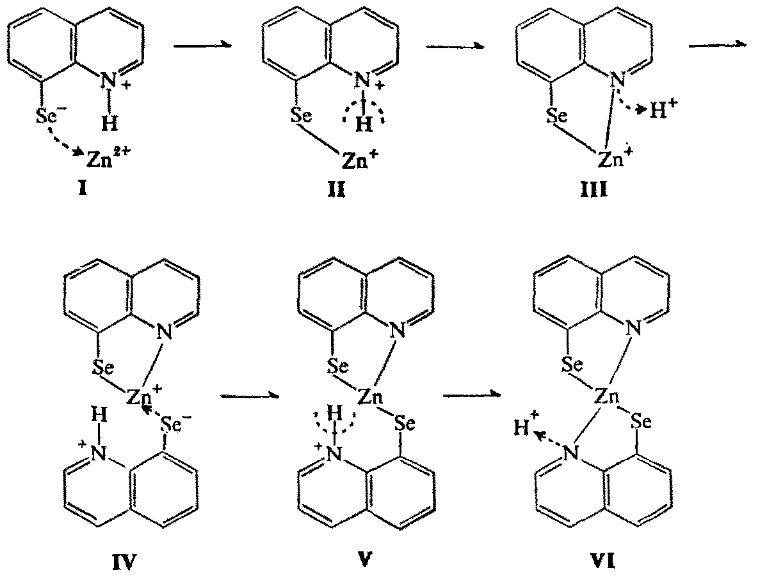
† R—C_9H_6NSe or C_9H_6NS.

‡ Precipitate from luteo salt solution, $Co(NH_3)_6^{3+}$.

8-mercaptoquinoline and 8-selenoquinoline complexes themselves. The order for the 8-hydroxyquinoline precipitates is almost the Irving-Williams order,[8] but that for 8-selenoquinoline and 8-mercaptoquinoline complexes is not.

Taking into account the electronegativities of selenium, sulphur and oxygen atoms, the covalent character of the metal–selenium bond is probably the same as or slightly greater than that of the metal–sulphur bond and is greater than that of the metal–oxygen bond. Therefore, copper(I), zinc and cadmium ions, classified as group B metals having filled *d* orbitals, will form the strongest covalent bonds, followed by copper(II), nickel and cobalt ions, which are the latter half of the first transition metal group having group B character. In addition to the covalent bond these metal ions, especially the group B metal ions, probably form π-bonds with the selenium or sulphur atom. Manganese, with increasing group A character forms a weak bond with selenium or sulphur, and alkaline earth metal and aluminium ions, being group A, do not form such complexes even in alkaline solution, although they do form complexes with 8-hydroxyquinoline.

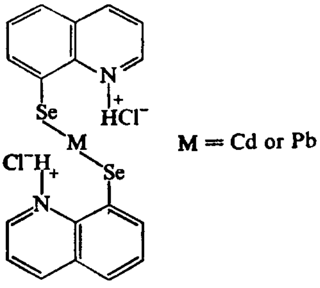
When zinc reacts with 8-selenoquinoline at $\text{pH} > 0{\cdot}75$, a hydrated zinc ion will approach the anionic selenium ($-\text{Se}^-$) of the zwitterion form of 8-selenoquinoline (step I), and will bond with it (step II). The value of pK_a corresponding to the dissociation of $\gt\text{N}-\text{H}^+$ is quite sensitive to the charge on the selenium atom.[9] That is, the neutralization of the selenium anion by a proton results in a remarkable decrease of the pK_a value from 8·75 to 3·26 as seen in Table II. Consequently, the formation of an Se–Zn bond makes the basicity of the nitrogen atom decrease significantly, so that the proton will dissociate at fairly low pH, and then the nitrogen atom will co-ordinate with the zinc ion even at pH 0·75 (step III). Then the second zwitterion form of 8-selenoquinoline approachs the 1:1 complex (step IV), and forms the second Se–Zn bond (step V), and then will complete the 1:2 complex (step VI).



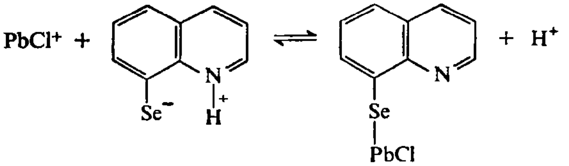
When the acidity of the solution increases, there is competition between zinc and hydrogen ions to bond with the nitrogen atom. At pH lower than 0·75 both Zn–N and Zn–Se bonds will be replaced by H–N and H–Se bonds respectively.

If the covalent character of an M–Se bond is higher than that of Zn–Se bond, for example Cd–Se or Pb–Se, the M–Se bond will still be preserved even if the M–N bond is replaced by an M–H bond. Consequently, in the case of cadmium and lead the red-orange precipitate of $MR_2 \cdot 2HCl$ as shown in formula I will be formed in a strongly acidic solution. The following reasons support the conclusion that the red-orange precipitate of cadmium is represented by formula I. (1) The theoretical weight of the precipitate is in the range of observed values. (2) This red-orange precipitate dissolves partly in hot water and then changes to a yellow-orange compound which may be the CdR_2 complex. (3) The metal-bonding infrared band for the 1:2 cadmium complex, CdR_2, 657 cm^{-1}, shifts to lower frequency, 645 cm^{-1}, for the red-orange compound. It is known that the metal-bonding bands which appear in the range of 600–700 cm^{-1} for the various metal 8-selenoquinoline and 8-mercaptoquinoline complexes shift to lower frequency when the chelate linkage is cleaved.[10] (4) The difference in colour of the two kinds of precipitate corresponds to the change of the visible absorption spectra of cadmium 8-selenoquinoline complex (1:1) in 50% dioxan–perchloric acid solution.[9]

In the case of lead, the existence of $PbR \cdot 2HCl$ in strongly acidic solution is confirmed by the same reasons as for cadmium. However, in addition to the formation of PbR_2 and $PbR_2 \cdot 2HCl$, the gray–green precipitate (of which the composition almost corresponds to $PbR \cdot Cl$) is formed in the range of pH 0·8–2·5. The following reaction will take place in this pH range, because the Pb–N bond is probably very weak:

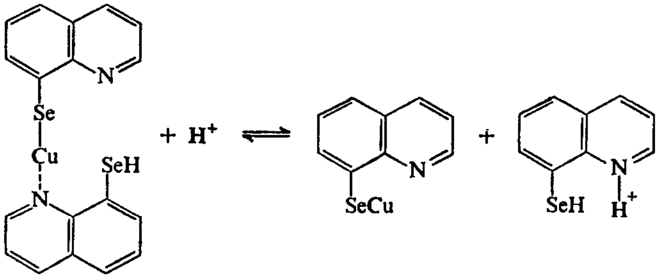


Formula I



If the M–Se bond and M–N bond are weaker than the Zn–Se bond and Zn–N bond respectively, for example in the manganese complex, the 1:2 complex will be formed at a higher pH than that for the formation of the zinc complex. That the stability of the manganese complex is less than that of other metal complexes is supported by the easy change to a white–brown substance even on gentle drying by heating.

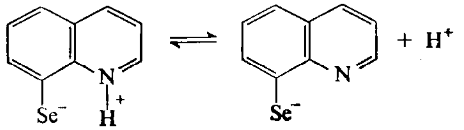
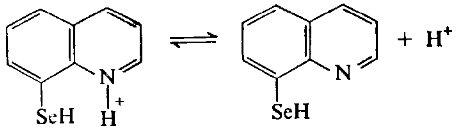
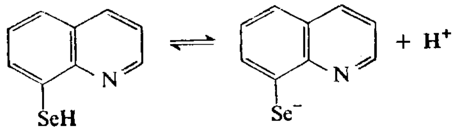
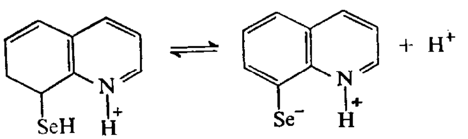
Copper(II) seems to be reduced to copper(I) by 8-selenoquinoline whether in the presence of hypophosphorous acid or not, as shown in Fig. 5. However, in the absence of hypophosphorous acid, the equivalent amount of 8-selenoquinoline required to reduce copper(II) to copper(I) is oxidized to 8,8′-diquinolyldiselenide which does not dissolve in the solution at pH $>$ 1·5. Thus the composition of the precipitate obtained with 8-selenoquinoline at pH $>$ 3·0 will be $\mathrm{CuR{\cdot}RH}$, not $\mathrm{CuR_2}$, and in strongly acidic solution the following dissociation will occur:



This supposition is supported by the following facts. (1) The observed weight of precipitate agrees with the theoretical. (2) This reaction occurs at pH below 2·9, which is slightly less than $\mathrm{p}K_{\mathrm{B}}$, 3·26, for the neutral form of 8-selenoquinoline in aqueous solution as shown in Table II.[4] (3) The precipitates obtained with and without hypophosphorous acid present both have a metal-indicative band at 656 cm^{-1} and in addition those obtained in its absence have a band at 642 cm^{-1}, which also appears with 8,8′-diquinolyldiselenide.

The weight of the precipitate of copper(I) 8-mercaptoquinoline complex, CuR formed in the pH range from about 0·5 to —0·55, almost agrees with the theoretical value. Of the metal ions dealt with in this study copper(I) will form the strongest

TABLE II.—ACID DISSOCIATION CONSTANTS FOR 8-SELENOQUINOLINE IN WATER.*

$\mathrm{p}K_{\mathrm{C}}$	8.75	
$\mathrm{p}K_{\mathrm{B}}$	3.26	
$\mathrm{p}K_{\mathrm{D}}$	5.41	
$\mathrm{p}K_{\mathrm{A}}$	—0.08	

---

* Reference 4.

covalent bond because it is extremely deformable. In fact, the 8-selenoquinoline complex precipitates completely at pH −0·88 (7·6*M* hydrochloric acid) and is 70% precipitated even from 12*M* hydrochloric acid. Similarly, 8-mercaptoquinoline complex precipitates in strongly acidic solution although no precipitate of CuR forms in 12*M* hydrochloric acid. If the $pH_{1/2}$ is defined as the pH at which the complex is 50% precipitated, the values of $pH_{1/2}$ for the 8-selenoquinoline and 8-mercaptoquinoline complexes are −0·95 and −0·71 respectively. This may be attributed to the covalent bond for Se–Cu being stronger than that for S–Cu.

The weight of the precipitate of the cobalt 8-selenoquinoline complex varies widely from the theoretical, and it is impossible to decide whether it is CoR_2, CoR·RH or CoR_3, as elemental analysis shows the composition to be highly variable and not corresponding to any of these formulae. The precipitates obtained from ammoniacal solution (pH 9–11) are almost constant in composition but do not correspond to CoR_3. Although the weight of the precipitate of the cobalt 8-mercaptoquinoline complex obtained at pH above 1·25 is not so variable as that of 8-selenoquinoline complex, it is not stoichiometric either.

Acknowledgement—The authors acknowledge the assistance of Mr. Y. Mido with the infrared measurements.

Zusammenfassung—Der Säureeinfluß auf die Fällung der Komplexe von 8-Selenochinolin und 8-Mercaptochinolin mit verschiedenen zweiwertigen Metallionen wurde systematisch untersucht und verglichen. Die verwendeten Metallionen waren Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} und Co^{2+}. Die meisten Metallionen außer Kupfer(II) und Kobalt(II) fallen als Komplexe mit dem Metall:Ligand-Verhältnis 1:2 aus. In salzsaurer Lösung fällt jedoch Cadmium als CdR_2·2HCl und Blei als PbR_2·2HCl oder PbR·Cl aus. Kupfer(II) wird zu Kupfer(I) reduziert und fällt bei einem pH über 2,0 als CuR_2·RH, in stark saurer Lösung als CuR aus. Kobalt(II) gibt keinen definiert zusammengesetzten Niederschlag; anscheinend fällt es als ein Gemisch aus CoR_2·RH und CoR_2 oder als andere Komplexe aus. Die Gründe für die Bildung der verschiedenen Niederschlagstypen werden erörtert.

Résumé—On a systématiquement étudié et comparé l'influence de l'acidité sur la précipitation de divers complexes de métaux divalents avec la 8-sélénoquinoléine et la 8-mercaptoquinoléine. Les ions métalliques étaient Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} et Co^{2+}. La plupart des ions métalliques, à l'exception du cuivre(II) et du cobalt(II), précipitent à l'état de complexe 1:2, métal:ligand. Toutefois, en solution dans l'acide chlorhydrique, le cadmium précipite à l'état de CdR_2·2HCl et le plomb à l'état PbR_2·2HCl on PbRCl. Le cuivre(II) est réduit en cuivre(I) et précipite à l'état CuR_2·RH à pH supérieur à 2,0 et à l'état CuR en solution fortement acide. Le cobalt(II) ne donne pas de précipité de composition définie mais précipite sous forme de mélange de CoR_2·RH et CoR_2 ou sous forme d'autres complexes. On considère les raisons de la formation des divers types de précipités.

REFERENCES

1. H. Goto, *J. Chem. Soc. Japan*, 1933, **54**, 725; 1935, **56**, 314.
2. V. I. Kuznetsov, Yu. A. Bankovsky and A. F. Ievin'sh, *Zh. Analit. Khim.*, 1958, **13**, 267, 507.
3. E. Sekido, Q. Fernando and H. Freiser, *Anal. Chem.*, 1963, **35**, 1550.
4. *Idem, ibid.*, 1964, **36**, 1768.
5. E. Sekido and I. Fujiwara, *Talanta, in* press.
6. N. Nakamura and E. Sekido, *ibid.*, 1970, **17**, 515.
7. A. Albert and A. Hampton, *J. Chem. Soc.*, 1956, 505.
8. H. Irving and R. J. P. Williams, *ibid.*, 1953, 3192.
9. E. Sekido, Q. Fernando and H. Freiser, *Anal. Chem.*, 1965, **37**, 1556.
10. Y. Mido and E. Sekido, *Bull. Chem. Soc. Japan*, 1971, **44**, 2130.

Talanta, 1972, Vol. 19, pp. 489 to 495. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF PHOSPHORUS IN HYPEREUTECTIC ALUMINIUM–SILICON ALLOYS

KOHICHI MUKAI
Nippon Light Metal Research Laboratory, Ltd., Kambara, Shizuoka, Japan

(*Received* 15 *June* 1971. *Accepted* 30 *August* 1971)

Summary—A reproducible method is described for determination of small amounts of phosphorus (from 0·0005% to 0·02%) in hypereutectic aluminium–silicon complex alloys. The method permits the separate determination of phosphorus in acid-soluble and acid-insoluble fractions. Phosphomolybdate is extracted with n-butanol–chloroform solvent mixture and back-extracted with a stannous chloride reducing solution. The phosphorus content of a sample cut into small pieces decreases during storage; loss of phosphorus is negligible on acid dissolution under oxidizing conditions.

ALUMINIUM–SILICON alloys are of considerable technical importance in casting processes. In casting of such alloys in the hypereutectic region, a uniform distribution of fine silicon particles in the material, which results in better tensile properties, is ensured by the addition of a small amount of phosphorus. The phosphorus reacts with the aluminium to produce aluminium phosphide, an efficient nucleating agent for the silicon. Since the amount of phosphorus retained in the alloys is of considerable metallurgical significance, an accurate method is required for the determination of this element, which is present in the form of aluminium phosphide both in the primary silicon particles and probably in the aluminium matrix.

The analytical method for the determination of phosphorus is usually based on the formation of phosphomolybdate or the corresponding reduced complex. Many basic investigations on these methods have been published.[1,2] Various methods have been developed for the determination of phosphorus in aluminium alloys, and found successful. However, the distillation separation of phosphorus in the acid-soluble fraction, as described by Kuhn,[3] is extremely laborious, and a direct photometric method for the determination of total phosphorus, described by Davey,[4] in which the alloys are dissolved in a nitric–hydrofluoric acid mixture, is simple but less reproducible and apt to give low results for the complex alloys. By Davey's method, of course, a separate determination of phosphorus in acid-soluble and acid-insoluble fractions is impossible.

Generally, hypereutectic aluminium–silicon complex alloys contain around 20% silicon, 1–2% copper, 1% magnesium, 1–1·5% nickel and/or 0·5% chromium. The phosphorus content is usually less than 0·01%.

The purpose of this study was to investigate an accurate and reproducible method for the separate determination of 0·0005–0·02% phosphorus in the acid-soluble and acid-insoluble fractions of hypereutectic aluminium–silicon complex alloys, as well as the errors caused by the form of the sample, period of storage and manner of dissolution.

The possibility of using emission spectrometric or X-ray fluorescence procedures for the total phosphorus was first considered. It was found, however, that in the case of the former there was interference from neighbouring iron or manganese lines with the phosphorus doublets at 253·5 and 255·4 nm and with the latter, interference with phosphorus K_α from copper $K_{\alpha 1}$ (fourth order). Therefore it was concluded that absorptiometric procedures were preferable.

Several authors have pointed out both silicon and aluminium can cause severe interference in the development of the phosphomolybdenum blue colour. In the present work, in order to obtain the most reproducible result, the silicon was removed completely and the phosphomolybdate was separated from aluminium by extraction with an organic solvent. On the basis of preliminary tests, phosphomolybdate was extracted with n-butanol–chloroform mixture and back-extracted with a stannous chloride reducing solution. This procedure has already been applied for the determination of phosphorus in copper,[5] lead[6] and pure iron[7] but not to aluminium alloys.

EXPERIMENTAL

Reagents

Standard phosphorus solution, 0·1 mg/ml. Dissolve 0·4263 g of diammonium hydrogen phosphate in water and dilute to 1 litre. Prepare working solutions by appropriate dilution.

Ammonium molybdate solution 10% w/v. Store in a polythene bottle for at least 24 hr before use.

Stannous chloride solution. Dissolve 1·5 g of $SnCl_2 \cdot 2H_2O$ in 5 ml of conc. hydrochloric acid, with heating, then dilute to 100 ml with water. Prepare just before use.

Solvent mixture. Mix 3 volumes of chloroform with 1 of n-butanol.

Recommended procedure

Transfer accurately about 0·5 g of the sample in massive form, each piece about 100 mg or more in weight and washed with acetone, to a 250-ml beaker. Add 30 ml of nitric acid (2 + 1) and 2 ml of conc. hydrochloric acid, cover with a watch-glass and heat gently. After the initial reaction has subsided, add further hydrochloric acid in two 4-ml portions to maintain a moderate rate of decomposition of the alloy. Avoid too rapid an addition and violent a reaction. Break the sample into smaller pieces with a glass rod to accelerate the dissolution if necessary.

After the dissolution, add 20 ml of water, filter through a Whatman No. 40 filter paper or equivalent, previously washed with 50 ml of warm 7*M* nitric acid and rinsed several times with hot water to guard against phosphorus contamination. Receive the filtrate in a 250-ml beaker. Wash the filter paper with hot water. Keep the black silicon residue for the determination of P in the acid-insoluble fraction.

Acid-soluble phosphorus content. Add 7 ml of perchloric acid (60%) and evaporate carefully to dryness until fumes are no longer evolved, on an asbestos pad on a hot-plate. This takes about 2 hr. Allow to cool, add 14 ml of 7*M* nitric acid and warm for about 5 min. Rinse the inside of the beaker with water. Add 5 ml of 3% EDTA solution, then heat to just below boiling and dissolve the residue. Transfer the solution to a 150-ml separatory funnel with water to make the final volume 50 ml. Add 4 ml of ammonium molybdate solution, mix and allow to stand for 5 min. Extract first with 20 ml and then 10 ml of solvent mixture, shaking for 3 min each time. Combine the extracts in another separatory funnel and add an appropriate volume of the stannous chloride reducing solution, (10 ml for <15 μg of P, 30 ml for <50 μg of P and 60 ml for <100 μg of P). Shake for 30 sec, allow to stand, discard the organic layer (bottom) and measure the absorbance of the blue colour against water in a 10-mm cell at 720 nm within 40 min from the addition of the stannous chloride solution.

If the blue solution is turbid, filter it through sanitary cotton plugged in the end of a separatory funnel.

Apply the whole procedure to a reagent blank determination, but with only 10 ml of 7*M* nitric acid, and subtract the absorbance from that of the sample.

For construction of the calibration curve, transfer 0–100 μg of P to separatory funnels, add 10 ml of 7*M* nitric acid, dilute to 50 ml with water, add 4 ml of ammonium molybdate solution and follow the procedure. Beer's law is obeyed up to at least 1·7 μg of P/ml and the molar absorptivity for phosphorus is $1 \cdot 39 \times 10^3$ l.mole^{-1}.mm^{-1}.

Acid-insoluble phosphorus content. Place the residue with the filter paper in a 50-ml platinum crucible. Add several drops of nitric acid, dry, and ignite at 600° until the paper has been burned. Remove from the flame and allow to cool. Add 5 ml of nitric acid (2 + 1) and 1 ml of perchloric acid (60%). Add hydrofluoric acid dropwise from a small polythene beaker, agitating the crucible during the addition, until all silicon has dissolved. Finally, add 3 ml of hydrofluoric acid and evaporate to dryness, until fumes are no longer evolved, on an asbestos pad on a hot-plate. Process a reagent blank in the same manner.

Cool and add 10 ml of 7*M* nitric acid and heat the contents of the crucible to nearly boiling. Transfer the resulting solution to a 150-ml separatory funnel with water and dilute to 50 ml. Add 4 ml of ammonium molybdate solution and treat as outlined above.

If only total phosphorus is required, add the resulting solution to the filtrate from the dissolution step, and apply the procedure.

RESULTS AND DISCUSSIONS

Form of sample

The form of sample used for determination of phosphorus is extremely important. If the sample is in the form of drillings, turnings or millings, a strong smell of gaseous phosphorus compounds is detected during machining. These finely divided samples give a low phosphorus result. Drillings of the hypereutectic aluminium–silicon complex alloys, for instance, gave a result which was lower by 0·006% than the true value of 0·021%. Therefore, the sample was cut into slices 2–3 mm thick from the cross-section of a test-piece, 80 × 10 × 40 mm book-type mould, or an ingot, with a clean saw-blade without lubricant, rapid cutting being avoided. The use of "as cast" surfaces should be avoided, since these are usually rich in phosphorus. When a sample slice, 0·5 g in weight and 2 mm in thickness, was cut into 5 pieces, the phosphorus content, decreased slightly to 0·019% from 0·020%.

TABLE I.—PHOSPHORUS CONTENT FOLLOWING LONG-TERM STORAGE

Sample	Form	P, % Oct. 1968	March 1970	Feb. 1971
A	Wafer	0·0038		0·0040
B	Wafer	0·0064		0·0063
C	Wafer	0·0069		0·0072
D	Wafer	0·0086		0·0085
E	Wafer	0·0144		0·0142
F	Book type		0·0043	0·0040
G	Book type		0·0082	0·0083
H	Book type		0·0167	0·0170

If sampling from a liquid alloy is possible, pour a small quantity of the molten alloy upon a clean, cold, smooth metal surface from a height of approximately 0·3 m. The resulting wafer of the alloy should be uniform and not more than 1 mm in thickness. The sample is cut off in pieces of suitable size just before analysis.

Stability of phosphorus in the alloy during storage

As stated above, phosphorus in the alloy seems to be unstable during machining. Absence of a standard aluminium-base alloy sample for phosphorus suggests the instability of this element on long-term storage. No work has been done on this problem, and confirmation of the stability of the phosphorus in the alloy during storage was necessitated.

Samples in wafer form and book-type form stored in paper envelopes had stable phosphorus content during storage for a year or more (Table I). On the other hand, the phosphorus content in samples cut into pieces (2 × 2 × 10 mm), even when stored in a desiccator, decreased gradually within a week as shown in Fig. 1.

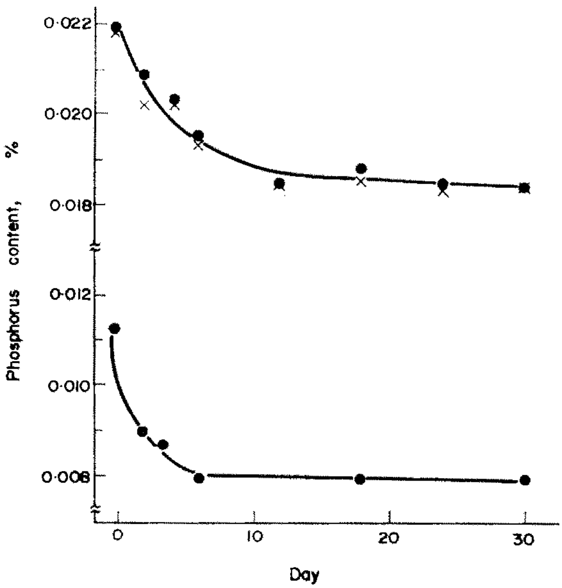


FIG. 1.—Phosphorus content in sample pieces over a period of a month.
●: Stored in desiccator ×: Left in atmosphere.

A sample of lower P content, 0·0076%, showed a slower decrease, to 0·0072% after a week.

Loss of phosphorus on acid dissolution

Phosphorus is readily liberated as phosphine by the action of nascent hydrogen. Kuhn's procedure[3] consists of absorbing (in brominated hydrobromic acid in a closed system) the phosphine liberated during hydrochloric acid attack upon the alloy. In Davey's procedure,[4] the alloy is completely decomposed by nitric–hydrofluoric acid mixture in an open system, which is quite simple to use compared with the closed system. Blackburn and Peters[8] confirmed by a neutron-activation method that the loss of phosphorus is negligible on complete dissolution of aluminium alloy in 3:1 nitric–hydrofluoric acid mixture but that a considerable amount of phosphine is released on use of hydrochloric acid. Mills *et al.*,[9] and Matelli and Vincentini,[10] however, still insisted upon hydrochloric acid dissolution in a closed system for the determination of phosphorus in the acid-soluble fraction. Pakalns,[11] for aluminium alloys with <2% silicon, adopted 10:3 nitric–hydrofluoric acid mixture for dissolving the sample for total phosphorus determination.

Because of the lack of precise descriptions, the manner of acid dissolution was evaluated again in terms of loss of phosphorus. Addition of 15 ml of 1:3 nitric–hydrochloric acid mixture and the same volume of water to 0·5 g of wafer sample (0·014% P) cut into pieces, did not cause any practical loss of P under rather vigorous reaction. In fact, in closed-system dissolution, less than 2 μg of P was found in the absorbing solution. In contrast, dissolution with 30 ml of hydrochloric acid (1 + 1) caused a remarkable loss of P in the acid-soluble fraction with a result 0·0024% lower than the true value of 0·0036%; nevertheless, in the acid-insoluble fraction the phosphorus content was almost the same as the result, 0·0104%, obtained by the

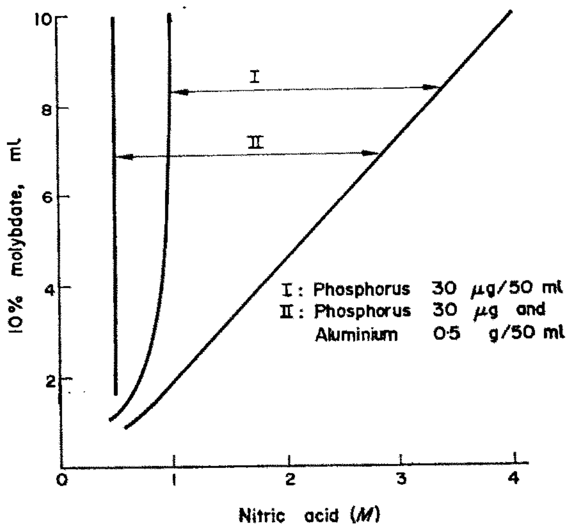


FIG. 2.—Optimum concentration ranges of reagents.

recommended procedure. To confirm the loss of P in the acid-soluble fraction, samples of pure aluminium in fine pieces, containing about 0·03% P, were dissolved under violent reaction conditions. The results obtained were 0·030% and 0·0015% of P from *aqua regia* and hydrochloric acid dissolution, respectively.

For a skilful analyst, not too much caution is required in dissolution of a slice sample under oxidizing conditions. In the present work, however, careful dissolution of a 0·5-g sample with 30 ml of nitric acid (2 + 1) and a total of 10 ml of conc. hydrochloric acid was adopted to prevent losses of phosphine as well as of spray. There is no need to use a distillation separation for the determination of phosphorus in the acid-soluble fraction.

Effect of concentration of nitric acid on extraction

Phosphate (30 μg of P) in a solution (50 ml) having an acidity of 0·3–2*M* with respect to nitric acid and containing 0·5 g of aluminium as nitrate, was subjected to the extraction and stripping procedure.

It was found that the optimum acidity before extraction is 0·6–1·7*M* in nitric acid when 4 ml of 10% ammonium molybdate solution are used, and that the extraction efficiency >95% in a single extraction from 0·8–1·3*M* nitric acid medium.

Generally, the range of optimum acid concentration depends on the amount of molybdenum solution added. This was reconfirmed in the present work and is shown in Fig. 2. However, in the determination of <5 μg of phosphorus, addition of too much ammonium molybdate should be avoided, because the resulting blue colour is unstable.

Stability of colour

The molybdenum blue obtained by the recommended procedure was stable at 20° for at least 40 min, after which the absorbance gradually decreased.

Influence of foreign ions

There is no known interference by alloying elements up to 2% or by the aluminium matrix. Certainly less than 5 mg of ionic Si, As and Ge have no influence. There is about 2 mg of Si in the acid-soluble fraction after acid dissolution of the alloys, and this is dehydrated by fuming in this procedure.

Among the impurity elements investigated, vanadium and zirconium decreased the absorbance if EDTA was not added. Commercial aluminium sometimes contains about 0·01% vanadium as impurity, but seldom contains more than 0·001% zirconium. There is no trouble caused by Zr at this level, but the presence of 0·05 or 0·1 mg of V causes a result low by 4 or 8 μg respectively in the determination of 10–50 μg of P. Addition of 5 ml of 3% EDTA solution prevents interference by up to 0·5 mg of V (equivalent to 0·1% V in the present work) or 2 mg of Zr if present.

TABLE II.—TYPICAL PHOSPHORUS RESULTS

Sample	Phosphorus, % Soluble fraction	Insoluble fraction	Total
1	0·0003	0·0020	0·0023
2	0·0002	0·0021	0·0023
3	0·0002	0·0030	0·0032
4	0·0003	0·0037	0·0039
5	0·0003	0·0048	0·0051
6	0·0003	0·0053	0·0056
7	0·0003	0·0065	0·0068
8	0·0005	0·0064	0·0069
9	0·0008	0·0072	0·0080
10	0·0006	0·0089	0·0095
11	0·0032	0·0065	0·0097
12	0·0037	0·0095	0·0132
13	0·0038	0·0106	0·0144
14	0·0026	0·0121	0·0147
15	0·0035	0·0120	0·0155
16	0·0024	0·0139	0·0163
17	0·0049	0·0120	0·0169

Contamination

Much care must be exercised at all times to avoid contamination, because there are many sources of microgram-level phosphorus contamination, such as cigarette ash, perspiration, filter paper and dust from fume hoods. All containers should be thoroughly rinsed both inside and out with 10% w/v ammonium hydrogen fluoride solution, and then with demineralized water. Clean samples and filter paper should not be handled with the naked fingers.

Determination of the phosphorus content

Typical results obtained on a number of aluminium–21% silicon complex alloy samples, covering a phosphorus range of 0·002–0·017%, are given in Table II. In general, most of the P existed in the acid-insoluble fraction. Phosphorus (0·0006%) was found in alloys made without addition of P, for in this case the metallic silicon contained 0·003% P.

The standard deviation was about 0·0002% for the range 0·001–0·010% of phosphorus. A set of 6 samples may be analysed in 6 hr for acid-soluble and acid-insoluble phosphorus. Reagent blank levels were of the order of 0·0002% P.

CONCLUSION

Conventional spectrophotometric methods available for the determination of phosphorus in separate fractions in hypereutectic aluminium–silicon complex alloys have been improved. Compared with the direct dissolution procedure, a little more time is consumed in processing the soluble and insoluble phosphorus fractions separately, but in this way, it is possible to correlate the phosphorus content of the two fractions with the properties of the alloy. It is possible, however, to combine the two fractions at a convenient stage before extraction and to obtain more reproducible and reliable results for total phosphorus without difficulty, because most of the silicon is preliminarily separated and removed by fuming.

Even on rather vigorous acid dissolution of the alloys containing a considerable amount of acid-soluble phosphorus, little loss of phosphorus was detected. The conditions used did not require a distillation separation to be made and so saved time.

It was also confirmed that the phosphorus in the alloys was stable over a long storage term unless the alloy was cut into small pieces.

The method may be extended to other aluminium-base alloys.

Acknowledgement—It is a pleasure to acknowledge the assistance given by Mr. S. Yagi and Mr. I. Izumi in the experimental work.

Zusammenfassung—Eine reproduzierbare Methode zur Bestimmung kleiner Phosphormengen (0,0005%–0,02%) in hypereutektischen Aluminium–Silicium–Mehrstofflegierungen wird beschrieben. Die Methode erlaubt die getrennte Bestimmung von Phosphor in säurelöslichen und säureunlöslichen Fraktionen. Phosphomolybdat wird mit einem Lösungsmittelgemisch aus n-Butanol und Chloroform extrahiert und mit einer Zinn(II)-chlorid-Reduktionslösung rückextrahiert. Der Phosphorgehalt einer in kleine Stücke zerteilten Probe nimmt bei der Aufbewahrung ab; beim Lösen in Säure unter oxidierenden Bedingungen ist der Verlust an Phosphor zu vernachlässigen.

Résumé—On décrit une méthode reproductible pour le dosage de petites quantités de phosphore (de 0,0005% à 0,02%) dans les alliages complexes aluminium-silicium hypereutectiques. La méthode permet la détermination séparée du phosphore dans les fractions acido-soluble et acido-insoluble. On extrait le phosphomolybdate par un mélange *n*-butanol-chloroforme, et extrait en retour avec une solution réductrice de chlorure stanneux. La teneur en phosphore d'un échantillon taillé en petites pièces décroît durant la conservation; la perte en phosphore est négligeable par dissolution acide dans des conditions oxydantes.

REFERENCES

1. D. F. Boltz, *Colorimetric Determination of Nonmetals*, p. 29. Interscience, New York, 1958.
2. S. R. Crouch and H. V. Malmstadt, *Anal. Chem.*, 1967, **39**, 1084.
3. M. V. Kuhn, *Fonderie*, 1958, **149**, 279.
4. M. L. Davey, *Metallurgia*, 1962, **65**, 151.
5. S. Yokosuka, *Bunseki Kagaku*, 1956, **5**, 395.
6. Japanese Industrial Standards, JIS H 1121-1961.
7. O. Kammori, I. Taguchi and T. Kayama, *Nippon Kinzoku Gakkaishi*, 1966, **30**, 78.
8. R. Blackburn and B. F. Peters, *Anal. Chem.*, 1963, **35**, 10.
9. E. C. Mills and S. E. Hermon, *Metal Ind., London*, 1962, **101**, 492.
10. G. Matelli and V. Vicentini, *Aluminio e Nuova Metallurgia*, 1969, **38**, 627.
11. P. Pakalns, *Anal. Chim. Acta*, 1970, **51**, 497.

Talanta, 1972, Vol. 19, pp. 497 to 503. Pergamon Press. Printed in Northern Ireland

ENHANCEMENT OF POLAROGRAPHIC REDUCTION CURRENTS BY A STATIC MAGNETIC FIELD

SHIZUO FUJIWARA and YOSHIO UMEZAWA
Department of Chemistry, Faculty of Science, University of Tokyo, Hongo 113, Tokyo, Japan

(*Received* 19 *June* 1971. *Accepted* 9 *September* 1971)

Summary—The effect of a magnetic field on d.c. polarographic reduction currents was studied with a static magnetic field applied perpendicularly to the dropping mercury electrode. In the presence of the magnetic field, diffusion or migration currents show a slight but distinct increase. The factors which can influence this effect have been examined experimentally. The effect is interpreted in terms of suppression of transfer of concentration polarization from one drop to the next. It is shown that certain types of maxima are enhanced by application of a magnetic field.

IT WAS FOUND in this laboratory that the maximum wave current in d.c. polarography decreases on application of a static magnetic field.[1,2] The decrease in current is always observable for the second kind of maxima, whereas for the first kind of maxima it occurs only with certain types of chemical systems. The magnetic field does not influence the drop-time and the flow-rate of mercury. The phenomenon has been interpreted in terms of retardation, by the magnetic field, of tangential motion at the surface of a mercury drop. The effect has also been examined in a.c. polarography[3] and oscillopolarography.[7]

In all these investigations[1–4] the magnetic field effect was to decrease the maximum wave current, and this can be interpreted in terms of magnetohydrodynamics. However, it has also been found[2] that a magnetic field causes a small *increase* in the limiting current. This paper gives the experimental details and interpretation of this effect, and shows that certain types of the maxima of the first kind are enhanced by the magnetic field. The effect of the magnetic field may be useful in elucidation of reaction processes at the surface of the dropping mercury electrode (DME).

EXPERIMENTAL

The d.c. polarograms were obtained with a Yanagimoto Polarograph Model PA-102 with a scan-rate of 0·2 V/min. Current-time curves during a single drop-life at fixed potential were obtained by using a potentiostat constructed in this laboratory and a spectrum computer (Model JRA-5, Japan Electron Optics Co.). A magnetic field of $5{\cdot}6 \times 10^5$ A/m was applied perpendicularly to the DME. The magnetic field is homogeneous within about 10 ppm over the whole volume of the glass cell. Some sample solutions were passed through a charcoal filter bed before measurement in order to eliminate surface-active substances. Potentials were measured *vs.* the mercury pool anode.

RESULTS AND DISCUSSION

The magnetic field often increases the limiting current by only a small amount (typically[2] 1 %) and can be observed only if the current is magnified to some extent. This enhancement implies that mass transport from the bulk solution to the electrode surface is increased by application of the magnetic field, presumably because of a stirring motion of electrolytes at the mercury/solution interface, brought about by the magnetic field. This statement is consistent with the results obtained by others. Leont'ev and Smirnov found that application of a magnetic field resulted in mixing of the electrolyte during electrolysis, which in turn caused a redistribution of cathodic current density.[5] Center *et al.* studied the effect of a magnetic field on electrolysis at a mercury pool cathode and found that the mercury/solution interface is hydrodynamically stirred by the magnetic field.[6] In the present system, it is assumed that the surface of a mercury drop is stirred hydrodynamically by a force F, defined as

$$F = JB \tag{1}$$

(where B is the magnetic field, and J the electrolytic current flowing at the mercury/solution interface) and that this results in an increase, in some cases, in mass transport to the electrode surface. The possibility that the force is due to direct interaction of the magnetic field with a diamagnetic mercury drop is considered very slight.

Effect on diffusion current

With the system 5mM lysine in 1M lithium chloride at pH 2·5, we observed a current minimum, *i.e.*, lowering of the diffusion current just after the fall of the maximum of the first kind; in the region of this current minimum, a magnetic field affects the current intensity appreciably as shown in Fig. 1. Similar results are observed for 1mM nickel or cobalt chloride with no supporting electrolyte. The current minimum following a maximum of the first kind has been studied by several workers,[7,8] and is attributed to the transfer of concentration polarization (TCP) from one drop to the next, which causes depletion of the depolarizer in the neighbourhood of the electrode. After the fall of the negative maximum (of the first kind, *i.e.*, a maximum which appears at a potential negative with respect to the electrocapillary zero potential), the depletion of the solution is especially enhanced,

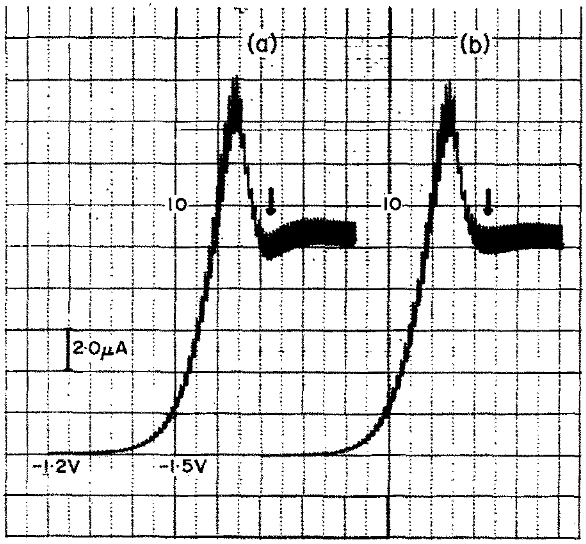


FIG. 1.—Effect of magnetic field on the minimum following the first kind of maximum.
5mM lysine and 1M LiCl, pH 2·5
(*a*): Without magnetic field
(*b*): Application of magnetic field

since at the maximum the depleted solution is transferred upwards and accumulates under the capillary in the vicinity of the drop, resulting in the current intensity being decreased after the maximum to less than the limiting diffusion current. Hence it may be concluded that the magnetic field can partially suppress the TCP, through the stirring action produced by F at the surface of the DME. This is consistent with the result obtained by Smoler,[7,9,10] who found that the current minimum does not appear when the capillary orifice is bent at an angle of 90° or 45°. He interpreted this in terms of removal of depleted solution from the capillary orifice, brought about by a falling drop. He observed a feeble downward streaming of the solution along the capillary orifice when the drop falls, which is a characteristic phenomenon of the inclined capillary and not observed in the case of the ordinary capillary.

As shown in Fig. 2, the magnetic field effect varies for different parts of the polarogram. It is most pronounced at the region of limiting diffusion current,

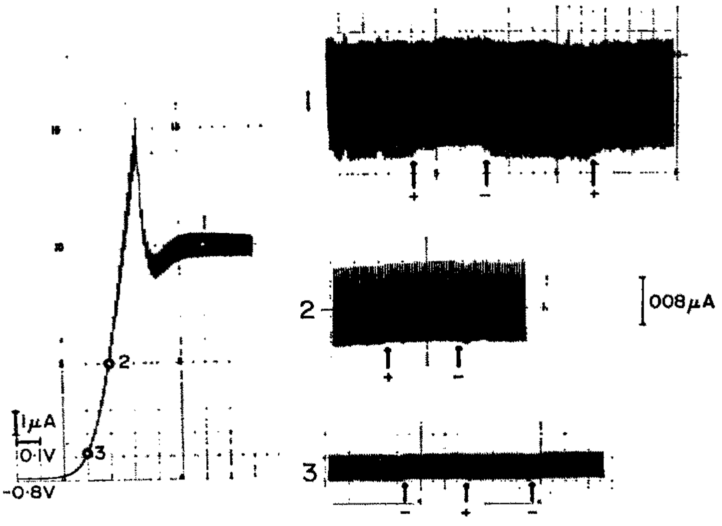


Fig. 2.—Comparison of magnetic field effect at various portions of the polarogram. 2mM $NiCl_2$ and no supporting electrolyte drop-time 3·49 sec (at −1·40 V, h = 0·70 m).
+: magnetic field switched on
—: magnetic field off
Sample solution was passed through a charcoal filter bed before measurement.

and almost imperceptible on the wave itself (as might be expected since depletion increases with wave-height). At the beginning of the wave the current is slightly *decreased* by the applied field (3 in Fig. 2).[2] The enhancement of the limiting diffusion current (1 in Fig. 2) is most marked at the beginning of growth of a mercury drop. This is consistent with the results of Hans *et al.* [11] who found the contribution from TCP is somewhat greater during the early growth of the drop. Because of difficulty in reproducing the hydrodynamic conditions,[7] the results are poorly reproducible, however (*cf.* Fig. 3).

Effect of surface-active substances. Addition of 0·001% of gelatin eliminates the increase in the limiting current caused by the magnetic field. It has been established[7,10] that the addition of surface-active substances lowers the TCP, and

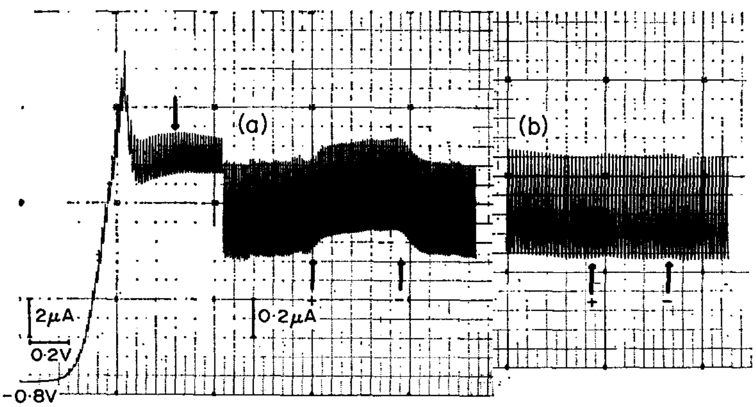


Fig. 3.—Effect of the drop-time on the magnetic field effect.
2mM NiCl$_2$ and no supporting electrolyte at −1·60 V (indicated by arrow on the d.c. polarogram)
(*a*): $t = 4{\cdot}28$ sec, (*b*): $t = 7{\cdot}87$ sec
+: magnetic field switched on
−: magnetic field off
Sample solution was passed through a charcoal filter bed before measurement.

this has been explained in terms of formation of a film of surface-active substance round the drop, this film being retained by the falling drop and carrying with it the depleted layer of the solution. As the surfactant has already suppressed the TCP, the magnetic field of necessity has no effect.

Influence of the drop-time. As shown in Fig. 3, the magnetic field enhancement of the limiting diffusion current is more pronounced when the drop-time is reduced. Smoler[7] found that the minimum after a negative maximum becomes more marked if the drop-time is shortened. When the drop grows slowly, the TCP effect is nullified because there is enough time for diffusion to occur. Rapid growth enhances TCP, which in turn is reduced by the magnetic field.

Concentration of supporting electrolyte. Increasing the concentration of supporting electrolyte diminishes the enhancement and may even cause a decrease in the limiting current when a magnetic field is applied. This may be explained as follows. TCP is expected to appear almost irrespective of the concentration of supporting electrolyte. However, addition of too much supporting electrolyte results in appearance of the second kind of maxima (which are due to the tangential motion brought about at the surface of a mercury drop by high flow-rate[9]). It has been shown that the second kind of maxima are reduced appreciably by application of a magnetic field.[2] According to Hans *et al.*[11] the second kind of maxima result in an increase in TCP (for the reasons given for the first kind). An increase in concentration of supporting electrolyte therefore results in formation of the second kind of maximum and then two opposing effects occur: (*a*) the effect of the magnetic field is enhanced because of the increase in TCP due to the maximum of the second kind, but (*b*) the magnetic field appreciably decreases the current of the second kind of maximum.

With the Smoler-type capillary, *i.e.*, a capillary inclined at 45°, the magnetic field decreased the limiting current when the concentration of supporting electrolyte was decreased, which can be explained in terms of the second kind of maxima, caused by the high flow-rate of mercury which is characteristic of this capillary.

The dependence of the magnetic field effect on the magnitude of current intensity, *i.e.*, a test of equation (1), was also studied. However, the results were poorly reproducible, because of differences in adsorbability of reaction products, which may determine the hydrodynamic conditions at the interface (*cf.* effect of surface-active substances, above).

Enhancement of the first kind of maxima

As shown in Fig. 4, (2mM uranyl sulphate, no supporting electrolyte), a maximum of the first kind may be enhanced appreciably by a magnetic field. Increasing the mercury head, however, increases the current at the maximum and the magnetic field effect becomes unobservable. A similar result is obtained for oxygen in $10^{-3}M$ potassium chloride with a trace of sodium polyacrylate, where the potential at which the maximum falls abruptly becomes more negative when the magnetic field is applied or the mercury head increased. This effect has been examined for a variety of chemical systems, but only a few show enhancement. Indeed, many show a decrease instead,[1,2] and their current–time curves during growth of a mercury drop fluctuate violently, that will be discussed elsewhere. The enhancement can be correlated with the anomalous shape of the current–time curve (*i–t* curve) during growth of a mercury drop at the maximum. For example, for 5mM copper(II) chloride in 0·1M ammonia–ammonium chloride, the current at the maximum increases with time, according to $i = Kt^{1/3}$, but falls abruptly at the later stages of drop growth until the diffusion current ($i = kt^{1/6}$) is attained (Fig. 5). A similar trend is observed for the uranyl sulphate and oxygen systems. The abrupt fall is probably due to formation of a weakly absorbed layer of surface-active substance,

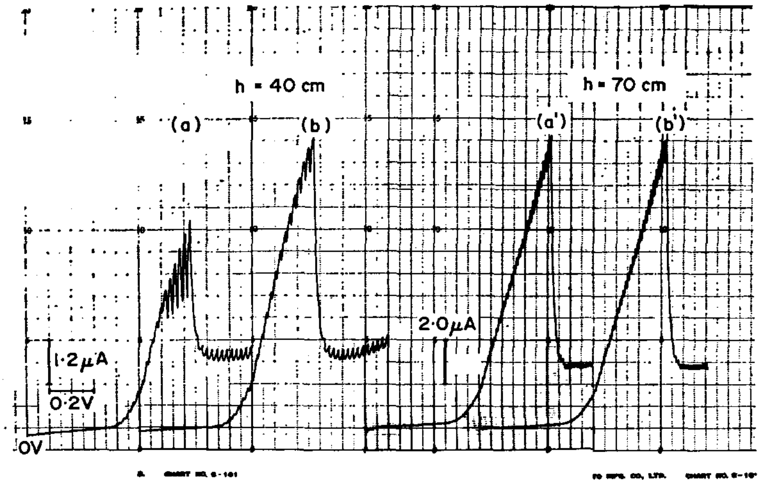


FIG. 4.—Relation between magnetic field effect on the first kind of maximum and mercury reservoir height *h*.
2mM UO_2SO_4 and no supporting electrolyte
(*a*), (*a*′): no magnetic field
(*b*), (*b*′): magnetic field on.

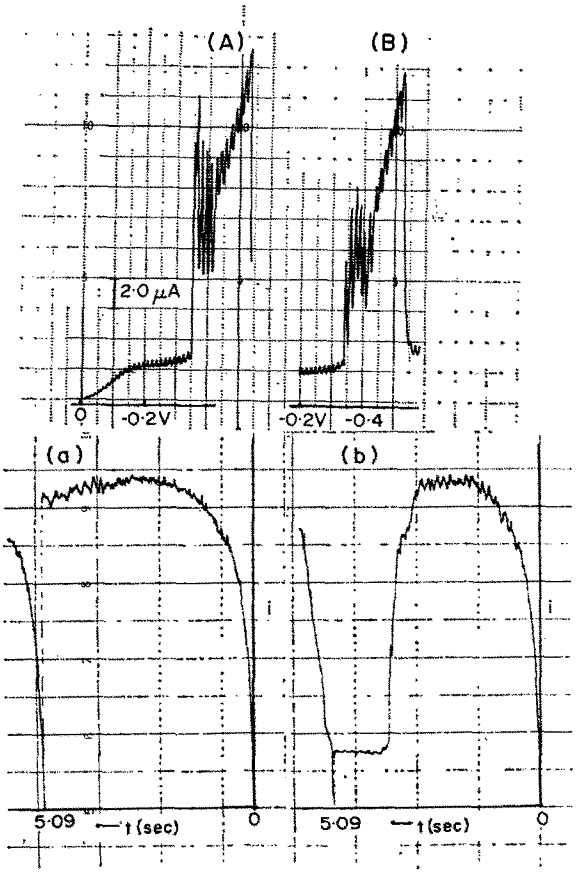


FIG. 5.—Relation between magnetic field effect on the first kind of maxima and the shape of the current-time curve at the maxima.
5mM $CuCl_2$ and 0·1M NH_3–NH_4Cl
Current-time curves are recorded at −0·42 V.
(*A*), (*a*): with magnetic field
(*B*), (*b*): no magnetic field

or an electrolysis product at the surface of the DME, resulting in disappearance of the maximum. Coverage of the surface of a DME by adsorbents is especially pronounced in the later stages of drop growth, the rate of expansion of surface area then being small.*

The magnetic field is clearly demonstrated in Fig. 5, the abrupt fall of the i–t curve being eliminated by the magnetic field. A possible explanation is that the force F disturbs the surface layer and removes any surface-active substances from the neighbourhood of the capillary orifice, resulting in a continuation of the current at a value $i = Kt^{1/3}$ until the drop falls. When the mercury head is increased, the abrupt fall of current is reduced by the increased rate of expansion of the surface area of the DME.

---

* The surface area A of the growing mercury drop can be represented as a function of time,[11] $A = kt^{2/3}$, and $dA/dt = \frac{2}{3}\,kt^{-1/3}$. From this it can be concluded that dA/dt becomes small with increase in t.

It appears that the present model for the effect of the magnetic field is reasonable; further study of this effect may be useful in exploration of the structure of the electrode double layer and the mechanism of transport phenomena at the DME.

Acknowledgement—The authors thank Teruhiko Kugo, Yanagimoto Co., Kyoto, for his valuable discussions and help in the experimental work.

Zusammenfassung—Der Einfluß eines Magnetfelds auf gleichstrom-polarographische Reduktionsströme wurde untersucht. Ein statisches Magnetfeld wurde senkrecht zur Quecksilbertropfelektrode angelegt. In Gegenwart des Magnetfeldes nehmen Diffusions- und Wanderungsströme um einen kleinen, aber deutlichen Betrag zu. Die Faktoren, die diesen Prozeß beeinflussen können, wurden experimentell untersucht. Der Effekt wird dadurch erklärt, daß die Übertragung der Konzentrationspolarisation von einem Tropfen zum nächsten unterdrückt wird. Es wird gezeigt, daß beim Anlegen eines Magnetfeldes bestimmte Typen von Maxima verstärkt werden.

Résumé—On a étudié l'effet d'un champ magnétique sur les courants de réduction polarographique en courant continu avec un champ magnétique statique appliqué perpendiculairement à l'électrode à goutte de mercure. En la présence du champ magnétique, les courants de diffusion ou de migration montrent un accroissement léger mais net. On a examiné expérimentalement les facteurs qui peuvent influer sur cet effet. L'effet a été interprété en fonction de la suppression du transfert de la polarisation de concentration d'une goutte à la suivante. On montre que certains types de maximums sont renforcés par l'application d'un champ magnétique.

REFERENCES

1. S. Fujiwara, H. Haraguchi and Y. Umezawa, *Anal. Chem.*, 1968, **40**, 249.
2. S. Fujiwara, Y. Umezawa and T. Kugo, *ibid.*, 1968, **40**, 2186.
3. S. Fujiwara, H. Kojima, Y. Umezawa and T. Kugo, *J. Electronal. Chem.*, 1970, **26**, 53.
4. S. Fujiwara, Y. Umezawa, T. Kugo and M. Hikasa, *Anal. Chem.*, 1970, **42**, 1005.
5. A. V. Leont'ev and A. G. Smirnov, *Tr. Kazansk. Khim-Teknol. Inst.*, 1964, No. 33, 36, *Chem. Abstr*, 1966, **65**, 1763C.
6. E. J. Center, R. C. Overbeck and D. L. Chase, *Anal. Chem.*, 1951, **23**, 1134.
7. I. Smoler, *J. Electroanal. Chem.*, 1963, **6**, 465.
8. L. Holleck, and A. M. Shams El Din, *J. Electroanal. Chem.*, 1968, **17**, 365.
9. J. Heyrovský and J. Kůta, *Principles of Polarography*, Academic Press, New York, 1966.
10. J. Kůta and I. Smoler, *Progress in Polarography*, Vol. I, p. 43. Interscience, New York, 1962.
11. W. Hans, W. Henne and E. Menrer, *Z. Elektrochem.*, 1954, **58**, 836.
12. G. S. Smith, *Nature*, 1949, **164**, 664.

Talanta, 1972, Vol. 19, pp. 505 to 513. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF WATER IN ORGANIC SOLVENTS WITH SOLVATOCHROMIC DYES—II*

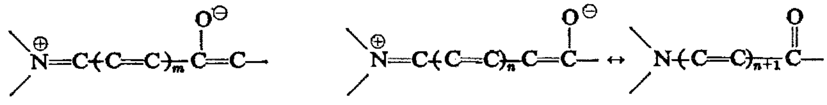
SADAKATSU KUMOI, HIROSHI KOBAYASHI and KEIHEI UENO®
Department of Organic Synthesis, Faculty of Engineering, Kyushu University,
Fukuoka 812, Japan

(*Received* 22 *June* 1971. *Accepted* 29 *September* 1971)

Summary—The correlation between the absorbance of a merocyanine dye in an organic solvent and the water content of the solvent has been investigated. The merocyanine dyes investigated are 1-methyl-4-[(4-oxo*cyclo*hexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine (I), 1-methyl-4-[(2-oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,4-dihydropyridine, 1-methyl-2-[(4-oxo*cyclo*hexa-2,5-dienylidene)-ethylidene]-1,2-dihydropyridine and 1-methyl-2-[(oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,2-dihydropyridine, and the organic solvents are isopropanol, acetone, acetonitrile and pyridine. The possibility of determining a trace amount of water in an organic solvent is demonstrated, and a procedure is proposed for the determination of trace water in pyridine. The sensitivity of the method depends on the solvent, being more sensitive in an aprotic solvent than in a protic one; for example, 0·05 or 0·27 mg of water in 1 ml of acetonitrile or of isopropanol respectively can be detected with I, by use of an ordinary spectrophotometer.

SINCE Kosower [1] attempted to define solvent polarity by the change in the position and intensity of absorption band of 1-alkylpyridinium iodide, several empirical parameters to characterize the solvent polarity have been proposed.[2–4]

The susceptibility of an absorption band to solvent polarity is known as solvatochromism, and marked solvatochromism is noticed especially in the charge-transfer band of a compound having a polarized structure in its ground state. The physicochemical basis of this phenomenon has been extensively studied.[5] Dyes and mixtures of dyes with betaine and merocyanine structures have been studied in various solvents.[6–9] A betaine dye in a ground state can be represented by a zwitterion structure, while a merocyanine dye is shown as a resonance hybrid of a zwitterion and an unpolarized structure in a solution.



$$\overset{\oplus}{\text{N}}{=}\text{C}\text{(}\text{C}{=}\text{C}\text{)}_m\overset{\text{O}^{\ominus}}{\overset{|}{\text{C}}}{=}\text{C}-$$

Betaine

$$\overset{\oplus}{\text{N}}{=}\text{C}\text{(}\text{C}{=}\text{C}\text{)}_n\overset{\text{O}^{\ominus}}{\overset{|}{\text{C}}}{=}\text{C}- \leftrightarrow \text{N}\text{(}\text{C}{=}\text{C}\text{)}_{n+1}\overset{\text{O}}{\overset{\|}{\text{C}}}-$$

Merocyanine

SCHEME 1

The polarity of organic solvents is affected by their water content and we reported the possibility of the determination of water in organic solvents by spectral change of some betaine dyes.[10] Similar determinations have been reported by others.[6–9] In this paper we consider the possibility of determining a minute amount of water in a range of organic solvents by the solvatochromatic effect of a group of merocyanine

---

* Contribution No. 245 from the Department of Organic Synthesis, Kyushu University. Part I, *Talanta*, 1970, **17**, 319.

dyes having homologous structures, such as 1-methyl-4-[(4-oxo*cyclo*hexa-2,5-dienylidene)-ethylidine]-1,4-dihydropyridine (4,4-M), 1-methyl-4-[(2-oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,2-dihydropyridine (4,2-M), 1-methyl-2-[(4-oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,2-dihydropyridine (2,4-M) and 1-methyl-2-[(2-oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,2-dihydropyridine (2,2-M). A procedure is proposed for the determination of trace water in reagent grade pyridine, and the sensitivities of water determination in various organic solvents with merocyanine dyes as well as betaine dyes are discussed in relation to the molecular structures of the dyes.

EXPERIMENTAL

Reagents

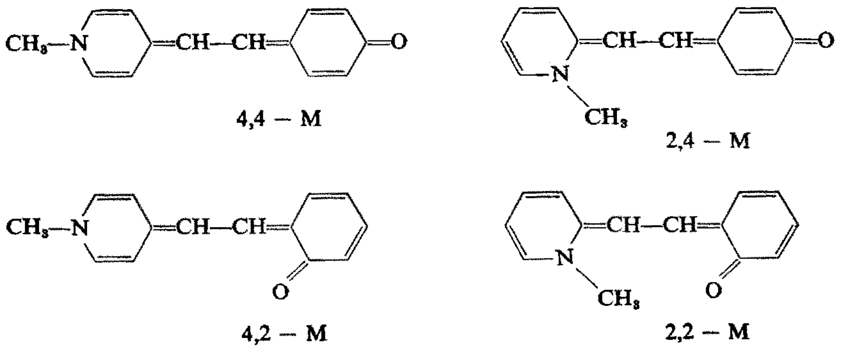
Solvatochromic dyes. The dyes used in this investigation are listed in Table I and their structural formulae in Fig. 1. The precursor hydroiodides were synthesized by the procedure of Phillips[11] and aqueous methanol solutions of the respective hydroiodides were treated on a column of hydroxyl-type anion-exchange resin to give the final merocyanine dyes, which were purified by recrystallization from aqueous acetone or methanol-acetone mixture. They were identified by elemental analyses and spectroscopy.

TABLE I.—APPEARANCES AND PROPERTIES OF SOLVATOCHROMIC DYES

Dye	Hydroiodide (solvent for recryst.)	Desiccated merocyanine dye*
4,4-M	red (water), m.p. 257–9°C	0·6 H_2O, violet†
2,4-M	yellow (methanol), m.p. 265°C	0·1 H_2O, deep green
4,2-M	violet needles (methanol) m.p 215–30°C	0·15 H_2O, greenish violet
2,2-M	yellow plates (methanol) m.p. 257–8°C	H_2O, green

* All the dyes showed no melting points, instead decomposing at various temperature above 200°C, depending upon the content of water of crystallization.

† S. J. Davidson and W. P. Jencks, *J. Am. Chem. Soc.*, 1969, **91**, 225.



4,4 – M 2,4 – M

4,2 – M 2,2 – M

FIG. 1.—Structures of merocyanine dyes.

In the solid state, they usually contained many molecules of water of crystallization. The desiccated samples were obtained by drying at 60°/10 nbar for 10 hr, but the last trace of water was very hard to remove.

Organic solvents. Isopropanol as a protic solvent and acetone, acetonitrile and pyridine as aprotic solvents were used. All were of reagent grade, and were dried by appropriate methods as summarized in Table II. The trace water content in each dried solvent was determined by Karl Fischer titration, the end-point being determined amperometrically.

TABLE II.—ORGANIC SOLVENTS AND THEIR WATER CONTENTS

Solvent	Method of drying	Water content of dried solvent, *mg/ml*
Isopropanol	reflux over calcium hydride	0·15
Acetone	reflux over Drierite	0·71
Acetonitrile	reflux over phosphorus pentoxide and over anhydrous calcium carbonate successively	0·45
Pyridine	reflux over potassium hydroxide pellets	0·41

Procedure for spectral study

The procedure was essentially the same as that described in the previous paper.[10] The stock solution for a dye was prepared so that the concentration was *ca.* $10^{-4}M$, and it was diluted to give the final solution, *ca.* $10^{-5}M$, in which the water content was determined.

Recommended procedure for determining trace water in pyridine with 4, 4-*M dye*

The stock dye solution was prepared by dissolving a weighed amount of dried 4,4-M dye (1·38 mg or 6·21 μmole) in dry pyridine to make 50 ml. A calibration curve of this dye was prepared by measuring the absorbance of pyridine solutions containing 2 ml of the stock dye solution and a known amount of water (50–250 mg) in 25 ml.

Two ml of the stock dye solution were transferred by pipette into a 25-ml dry volumetric flask, and made up to the mark with a pyridine sample of unknown water content. After mixing, solution was transferred into an air-tight spectrophotometric cell for absorption measurement at 610 nm against distilled water. Another 5-ml aliquot was transferred into a titration cell for determination of the water content by Karl Fischer titration. The results are summarized in Table III.

TABLE III.—DETERMINATION OF WATER CONTENT IN REAGENT GRADE PYRIDINE BY SPECTROPHOTOMETRIC METHOD AND KARL FISCHER TITRATION METHOD

Sample	Absorbance at 610 nm*	Water content, *mg/ml*	
		Spectrophotometric method†	Karl Fischer titration
Dry pyridine	0·748	—	0·32
No. 1	0·723	0·80	0·80
No. 2	0·647	2·7	2·60
No. 3	0·578	4·7	5·11

* The final dye concentration was $9{\cdot}95 \times 10^{-6}M$.

† The dry pyridine used in preparation of calibration curve was found to contain 0·32 mg of water per ml by Karl Fischer titration. Therefore, the calibration curve was connected for this amount.

RESULTS AND DISCUSSION

Applicability of the dyes

Before quantitative evaluation, applicability of the dyes to trace water determination was checked in respect to their solubilities in various organic solvents, chemical stabilities and analytical sensitivities. The solubility had to be at least $10^{-4}M$ for the preparation of the stock solution. Table IV summarizes the dissolution behaviour of the dyes in the solvents used, including water.

TABLE IV.—DISSOLUTION BEHAVIOR OF THE DYES

Dye	Solvent				
	Water	Isopropanol	Acetonitrile	Pyridine	Acetone
4,4-M	good*	good	fair†	good	poor‡
2,4-M	good	good	good	good	fair
4,2-M	good	good	fair	poor	poor
2,2-M	good	good	good	good	fair

* good: sufficiently soluble for absorption spectrophotometry.
† fair: sufficiently soluble but dissolving slowly.
‡ poor: insufficiently soluble or insoluble.

Generally the dyes were fairly soluble in a protic solvent, and the dyes 2,4-M and 2,2-M were soluble enough in the protic and aprotic organic solvents so far studied. Water determination in this work was carried out in isopropanaol, acetonitrile and pyridine, acetone being excluded because of its poor dissolving power for the dyes.

The dyes were chemically stable and not photosensitive in solution, but they appeared to exhibit a stronger thermochromic effect[12,13] than the betaine dyes reported earlier,[10] though no systematic investigation was carried out. Therefore, analytical operations were carried out under an ordinary fluorescent lamp and photometric measurements were performed at a temperature as invariable as possible.

Quantitative evaluation of the dyes

The dyes were evaluated by comparing the spectral change in an organic solvent containing a known amount of water. Figure 2 shows the visible absorption spectra of 4,4-M in isopropanol and in acetonitrile. Substantial changes in the spectra can be observed with the change of water content in the range of 0–20 mg/ml for isopropanol and 0–10 mg/ml for acetonitrile. The spectral change observed in pyridine is of intermediate degree.

The change in absorbance at certain wavelengths (560 and 570 nm for isopropanol and 580 nm for acetonitrile) when plotted *vs.* water content gives calibration curves for the determination of water, as shown in Fig. 3. The curves are not necessarily linear, because the method is not based on Beer's law.

Figure 4 shows the absorption spectra of dye 2,4-M in aprotic solvents such as acetonitrile and pyridine. Again acetonitrile gives the strongest spectral change, that in isopropanol being of similar to that in pyridine. When the change of absorbance at 550 and 560 nm is plotted against the water content, calibration curves for the range 0–10 mg/ml are obtained.

In order to compare analytical sensitivities of the dyes, we define the sensitivity as $S = \Delta A/\Delta W$, where ΔA is the change in absorbance for a change of water content of ΔW.* S-values of the dyes are summarized in Table V, as are the analytical limits of detection, D, defined by $D = 0{\cdot}004/S$, the coefficient 0·004 being based on the fact that an ordinary spectrophotometer can measure absorbance with a precision of ±0·002. Table V indicates that the S-value is generally higher in aprotic than in protic solvents.

---

* In the previous paper,[10] the term "sensitivity, S" was the inverse of that used here, and corresponds to the limit of detection D. Also the equation[10] defining S was misprinted, and should be corrected to $S = 0{\cdot}004\Delta W/\Delta A$. S is now redefined (at the suggestion of the referee), since it seems more sensible that a large S value should mean a higher sensitivity.

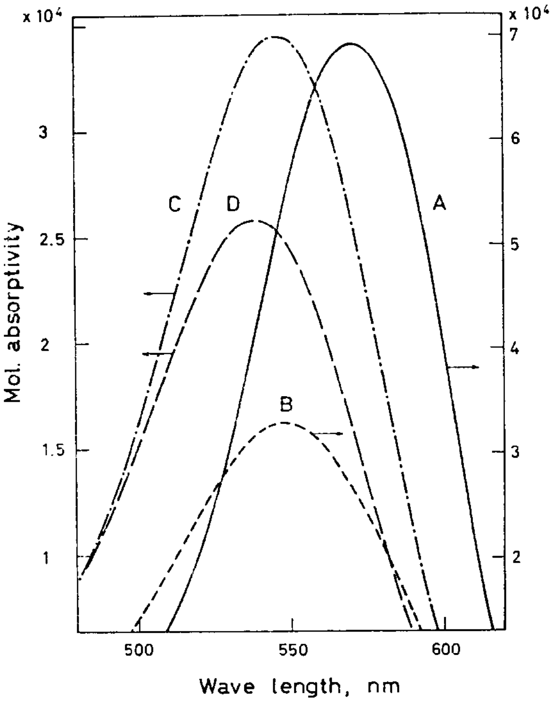


FIG. 2.—Visible absorption spectra of 4,4-M.
(A) in dried acetonitrile
(B) in acetonitrile containing an additional 10 mg of water per ml of the solvent
(C) in dried isopropanol
(D) in isopropanol containing an additional 20 mg of water per ml of the solvent.

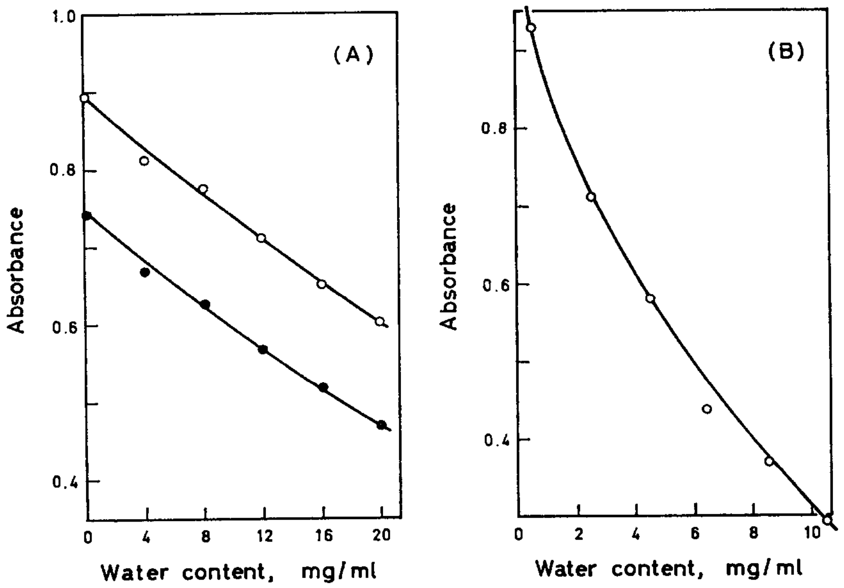


FIG. 3.—Calibration curves for water determination with 4,4-M.
(A) in isopropanol, dye concentration $2{\cdot}82 \times 10^{-5}M$. ○: measured at 560 nm; ● at 570 nm
(B) in acetonitrile, dye concentration $1{\cdot}39 \times 10^{-5}M$.

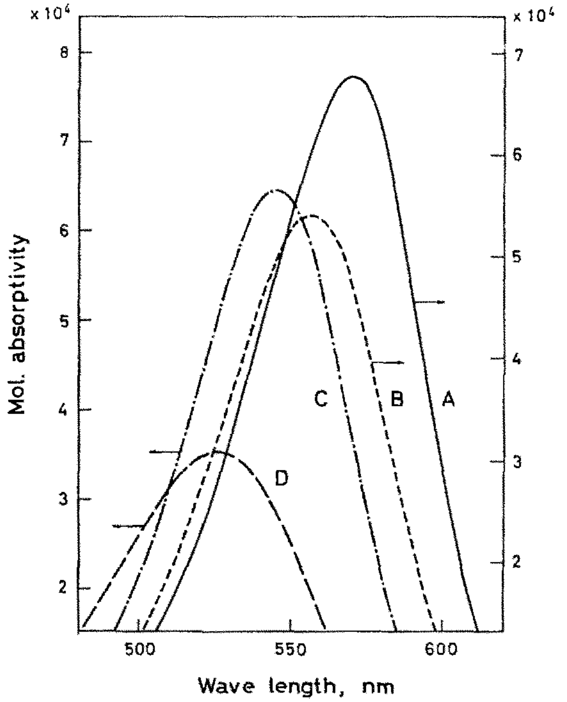


FIG. 4.—Visible absorption spectra of 2,4-M.

(A) in dried pyridine
(B) in pyridine containing an additional 20 mg of water per ml of the solvent
(C) in dried acetonitrile
(D) in acetonitrile containing an additional 10 mg of water per ml of the solvent.

TABLE V.—SENSITIVITY, *S*, OF WATER DETERMINATION

Solvent	Dye	ΔA	ΔA *mg/ml*	*S*, *ml/mg*	*D*, *mg/ml*	λ, *nm*
Isopropanol	4,4-M	0·291	20	0·015	0·27	560
	2,4-M	0·250	20	0·013	0.32	540
	4,2-M	0·232	20	0·012	0·34	570
	2,2-M	0·138	20	0·007	0·58	540
Acetonitrile	4,4-M	0·493	6	0·082	0·05	580
	2,4-M	0·357	6	0.059	0.07	550
	4,2-M	0·365	6	0·061	0.07	610
	2,2-M	0.232	6	0·039	0·10	570
Pyridine	4,4-M	0.290	10	0·029	0.14	610
	2,4-M	0.253	12	0·021	0·19	590
	4,2-M	0.260	12	0·022	0·18	640
	2,2-M	0.309	12	0·026	0·15	600

Dye 4,4-M is the most sensitive for both protic and aprotic solvents. Dye 2,2-M exhibits the poorest sensitivity, half that of dye 4,4-M. Dyes 2,4-M and 4,2-M show similar analytical sensitivities midway between those of the other two.

Determination of trace water in pyridine

As a typical example, the proposed procedure was applied to the determination of a trace amount of water in reagent grade pyridine, and the result was compared with that obtained by the Karl Fischer titration method.

In this procedure, the dye concentration has to be kept constant for the standard solutions employed in the preparation of calibration curve as well as for the samples. Therefore, it is desirable to use the same stock dye solution for both purposes, because the same volume of stock solution can be used in preparing the final solutions throughout the procedure. As 2 ml of dye solution could be manipulated fairly accurately, a satisfactory reproducibility was obtained by the proposed method. It does not seem necessary to use a non-solvachromic dye as an internal standard to correct the solvatochromic dye concentration, such as was proposed in our previous paper.

As it was noticed that these dyes showed a noticeable thermochromism, the calibration and sample measurements should be done at the same temperature. Accordingly, our experiments were carried out in a constant-temperature room.

Table III shows fairly good agreement between the results obtained by the two methods. However, the dry pyridine used in the preparation of the calibration standard was found to contain 0·32 mg of water per ml by the Karl Fischer method, and the calibration curve had to be corrected.

As discussed previously, the method is not as sensitive as the Karl Fischer method, and is subject to interference by polar impurities. However, the procedure is far simpler than the titrimetric method, and may find wide application.

Correlation of S-value with molecular structure of the dye

Table VI lists the *S*-values of the betaine dyes, which are the most sensitive to water content among those investigated in the previous work,[6] including the 4,4-M merocyanine dyes for comparison. In aprotic solvents these dyes show comparable sensitivities for water determination. In protic solvents, however, the merocyanine dye is much more sensitive. Thus, at present, the 4,4-M has a wider applicability than the betaine dyes.

TABLE VI.—COMPARISON OF *S*-VALUES OF THE BETAINE AND MEROCYANINE DYES

Dye	Solvent		
	Isopropanol	Acetonitrile	Pyridine
P-2*	0·004	0·040	0·017
1,6-Q†	0·004	0·067	0·030
4,4-M	0·015	0·082	0·029

* 2,4,6-triphenyl-*N*-(3,5-diphenyl-4-hydroxyphenyl)-pyridinium betaine.

† 1-methyl-6-hydroxyquinolinium betaine.

In the dye molecules the distance between the cationic (R_3N^+) and anionic (RO^-) centres in the zwitterion structure is considered to increase in the order 2,2-M < 4,2-M $\sim$ 2,4-M < 4,4-M, though a definite conformation of the dye molecule in solution is not clear. This order parallels the increase in S-values. A similar relationship is also observed with the betaine dyes, 1,6-Q, 1,8-Q (1-methyl-8-hydroxyquinolinium betaine) and 2,5-IQ (2-methyl-5-hydroxyisoquinolinium betaine),[10] in which distances between oppositely polarized sites on aromatic nuclei are definite.

Results of the measurements of transition energy, E_T, of the merocyanine dyes in various solvents are tabulated in Table VII. Plots of E_T (measured in the protic solvents) *vs.* $f(\varepsilon)$ were linear, with slopes of 163·8, 146·8 and 140·1 for 4,4-M, 4,2-M and 2,2-M respectively, giving the spectral susceptibility of the dye to solvent polarity. The dye 4,4-M is the most susceptible, indicating it should have the highest solvatochromic effect among the four dyes. In aprotic media a similar tendency can be observed.

TABLE VII.—TRANSITION ENERGY, E_T, OF MEROCYANINE DYES IN VARIOUS SOLVENTS

Protic solvent	ε	$f(\varepsilon)$	E_T, *kJ*. mole^{-1}			
			4,4-M	2,4-M	4,2-M	2,2-M
Water	78·5	0.982	271	—*	266	274
Methanol	32·6	0·954	247	254	245	251
Ethanol	24·3	0·940	233	240	233	240
n-Propanol	20·1	0·928	228	235	227	236
Isopropanol	18·3	0·920	218	227	218	231
n-Butanol	17·1	0·914	225	231	226	235
Aprotic solvent						
Acetonitrile	37·5	0·960	209	219	206	216
Acetone	20·5	0·928	201	214	196	209
Pyridine	12·3	0·882	197	210	193	206

ε: Dielectric constant of solvent, $f(\varepsilon) = 2(\varepsilon - 1)/2\varepsilon + 1$.

E_T: Transition energy.

* λ_{max} is not clear on the absorption spectra of 2,4-M dye in aqueous solution.

These results suggest that in a group of dyes having homologous polar structures the extent of the solvatochromic effect depends upon the distance between the oppositely polarized sites, which presumably affects the difference between the dipole moments of a dye molecule in the ground and excited states. A larger blue shift, however, would not necessarily be obtained with longer distance between the oppositely polarized sites in a dye molecule. There must be an optimal distance for a certain chromophore system.

Analytical sensitivity is not solely dependent upon the gradient, $\Delta E_T/\Delta f(\varepsilon)$. For example, despite the S-value ratio of 4,4-M to 2,2-M being about 2:1, the gradient, $\Delta E_T/\Delta f(\varepsilon)$, for the former is only 15% steeper than that for the latter. Another example is presented in Table VIII, which shows the spectral change of 1,6-Q betaine and 4,4-M merocyanine in isopropanol. Although both dyes show a virtually equal extent of blue shift with an equal increase of water content, the hypochromic shift with water content of the latter dye is several times that of the former. In comparison with the merocyanine dyes, the betaine dyes generally show a rather small change in intensity at absorption maximum with increase of water content. The S-value depends upon the spectral shift in terms of both wavelength and absorption intensity.

TABLE VIII.—SPECTRAL CHANGE OF 1,6-Q AND OF 4,4-M IN ISOPROPANOL

Dye	λ_{max} *nm*		$\Delta\lambda$,† *nm*	A‡		ΔA§
	I*	II*		I	II	
1,6-Q	460	453	7	1·000	0·980	0·020
4,4-M	546	539	7	1·000	0·750	0·250

* Aliquot I is of a dried solvent, II contains an additional 2% of water.

† $\Delta\lambda = \lambda_{max}(I) - \lambda_{max}(II)$.

‡ A: absorbance at λ_{max}.

§ $\Delta A = A(I) - A(II)$.

The higher sensitivity of the merocyanine dye in protic solvents is mainly due to the change in absorption intensity.

Acknowledgement—The authors wish to thank the Ministry of Education for financial support of this work.

Zusammenfassung—Die Beziehung zwischen der Extinktion eines Merocyaninfarbstoffs in einem organischen Lösungsmittel und dem Wassergehalt des Lösungsmittels wurde untersucht. Die untersuchten Farbstoffe sind 1-Methyl-4-[(4-oxo*cyclo*hexa-2,5-dienyliden)-äthyliden]-1,4-dihydropyridin (I), 1-Methyl-4-[(2-oxo*cyclo*hexa-3,5-dienyliden)-äthyliden]-1,4-dihydropyridin, 1-Methyl-2-[(4-oxo*cyclo*hexa-2,5-dienyliden)-äthyliden]-1,2-dihydropyridin und 1-Methyl-2-[(2-oxo-*cyclo*hexa-3,5-dienyliden)-äthyliden]-1,2-dihydropyridin, die organischen Lösungsmittel Isopropanol, Aceton, Acetonitril und Pyridin. Es wird gezeigt, daß man eine Spurenmenge Wasser in einem organischen Lösungsmittel bestimmen kann; eine Vorschrift zur Bestimmung von Wasserspuren in Pyridin wird vorgeschlagen. Die Empfindlichkeit des Verfahrens hängt vom Lösungsmittel ab, sie ist in einem protonenfreien Lösungsmittel höher als in einem protonenhaltigen. Z. B. kann man mit I in einem gewöhnlichen Spektrophotometer in 1 ml Acetonitril oder Isopropanol 0,05 bzw. 0,27 mg Wasser nachweisen.

Résumé—On a étudié la corrélation entre l'absorption d'un colorant de type merocyanine dans un solvant organique et la teneur en eau du solvant. Les colorants de type merocyanine étudiés sont les 1-méthyl 4-[(4-oxo*cyclo*hexa-2,5-diénylidène)-éthylidène] 1,4-dihydropyridine (I), 1-méthyl 4-[(2-oxo*cyclo*hexa 3,5-diénylidène)-éthylidène] 1,4-dihydropyridine, 1-méthyl 2-[(4-oxo*cyclo*hexa 2,5-diénylidène)-éthylidène] 1,2-dihydropyridine, et 1-méthyl 2-[(2-oxo*cyclo*hexa 3,5-diénylidène)-éthylidène] 1,2-dihydropyridine, et les solvants organiques sont l'isopropanol, l'acétone, l'acétonitrile et la pyridine. La possibilité de détermination d'une trace d'eau dans un solvant organique est démontrée, et l'on propose une technique pour le dosage de l'eau à l'état de traces dans la pyridine. La sensibilité de la méthode dépend du solvant, étant plus sensible dans un solvant aprotique que dans un solvant protique; par exemple, on peut détector 0,05 our 0,27 mg d'eau dans 1 ml d'acétonitrile ou d'isopropanol, respectivement, au moyen de (I), en utilisant un spectrophotomètre ordinaire.

REFERENCES

1. F. M. Kosower, *J. Am. Chem. Soc.*, 1958, **80**, 3253, 3267.
2. C. Reichardt, *Angew. Chem. (Intern. Ed.)* 1965 **4**, 29.
3. T. Kagiya, T. Sumida and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.
4. K. Dimroth and C. Reichardt, *Ann.*, 1969, **727**, 93.
5. W. Liptay, *Angew. Chem. (Intern. Ed.)*, 1969, **8**, 177.
6. L. G. S. Brooker, G. H. Keyes and D. W. Heseltine, *J. Am. Chem. Soc.*, 1951, **73**, 5350.
7. K. Dimroth and C. Reichardt, *Z. Anal. Chem.*, 1966, **215**, 344.
8. J. P. Phillips and R. W. Keown, *J. Am. Chem. Soc.*, 1951, **73**, 5483.
9. C. Reichardt, *Ann.*, 1968, **715**, 74.
10. S. Kumoi, K. Oyama, T. Yano, H. Kobayashi and K. Ueno, *Talanta*, 1970, **17**, 319.
11. A. P. Phillips, *J. Org. Chem.*, 1947, **12**, 333; 1949, **14**, 302.
12. J. H. Day, *Chem. Rev.*, 1963, **63**, 65.
13. K. Dimroth, C. Reichardt and A. Schweig, *Ann.*, 1963, **669**, 95.

Talanta, 1972, Vol. 19, pp. 515 to 525. Pergamon Press. Printed in Northern Ireland

YIELDS OF PHOTONUCLEAR REACTIONS FOR PHOTON-ACTIVATION ANALYSIS WITH HIGH-ENERGY BREMSSTRAHLUNG

TOYOAKI KATO and YOSHINAGA OKA*
Department of Chemistry, Faculty of Science, Tohoku University,
Sendai, Japan

(*Received* 7 *June* 1971 *Accepted* 16 *September* 1971)

Summary—Experimental reaction yields have been determined for various types of photonuclear reactions, induced in 52 elements by means of Bremsstrahlung irradiation with maximum energies ranging from 30 to 72 MeV, and of detection of the resultant activities with a lithium-drifted germanium detector. From the results obtained, sensitivities in photon-activation analysis were evaluated and the reactivity of high-energy photons with nuclei in a wide range of atomic number is discussed. Some nuclear considerations in photon-activation analysis, involving the relative probability of forming each product as a result of the (γ,$xn\gamma p$) reactions are also given.

IN RECENT YEARS photon-activation analysis has been exploited as a useful analytical method for the determination of trace amounts of a number of elements in the periodic table. A cyclic or linear electron accelerator capable of producing a high-current electron beam has been used as the irradiation facility, and several reports concerning the experimental or calculated sensitivities with bremsstrahlung of moderate maximum energies (~35 MeV) have been published.[1-6] Sensitivities well below 1 μg are obtained for many elements, and the emphasis is on the determination of those elements having nuclear properties unfavourable for thermal-neutron activation analysis, such as carbon, nitrogen, oxygen and fluorine. These elements can also be determined at very low levels by means of charged-particle activation analysis. In addition, severe difficulties due to sample self-shielding are encountered when a mixture to be analysed contains substantial amounts of elements with large thermal-neutron capture cross-sections. In these cases, photon-activation analysis is found to be very promising.

A general feature of the photon absorption cross-section for a nucleus is characterized by a peak 5–6 MeV wide at an energy located between the photodisintegration threshold and about 30 MeV, and, in this energy region, the main nuclear events are the emission of one neutron or one proton. A considerable amount of work has been done in the past on the determination of the (γ,n), (γ,p) and (γ,α) reaction yields for many elements with Bremsstrahlung produced by 20-MeV electons.[7-9]

Since yield is a function of photon energy, it should be noted that higher sensitivities can be expected with an accelerator giving Bremsstrahlung of higher maximum energies. The excitation of a nucleus by gamma-rays with higher energies, however, gives rise to more complex events. Apart from the reactions described above, those with the emission of two or more nucleons become important, thereby causing difficult interference problems in photon-activation analysis. A basic problem in photon-activation analysis under such conditions is, therefore, the necessity to investigate the production rates or yields of various photonuclear reactions induced

---

* Present address: Department of General Education, Kitasato University, Sagamihara, Kanagawa, Japan.

simultaneously in a sample to be analysed, over the energy range of given bremsstrahlung. It should also be mentioned that the production rates of those reactions depend on a specific target-sample configuration used for activation. Recently, Engelmann[10] determined the distribution of the 25–45 MeV electron-induced Bremsstrahlung beam spectrum by activating silver and carbon monitors arranged behind platinum and aluminium targets, and the longitudinal and transverse distribution patterns have been presented in terms of amounts of (γ,n) activation.

The work described here was undertaken in order to evaluate the potential for determining trace amounts of many elements by inducing the (γ,$xnyp$) reactions with bremsstrahlung from a linear electron accelerator and by detecting the resultant activities with a lithium-drifted germanium detector. Thus, first, sensitivities were obtained for some 13 elements at two different Bremsstrahlung maxium energies, 30 and 60 MeV, and secondly, the yield values at 30 MeV for 138 different reactions were obtained and discussed in terms of some nuclear considerations for photon-activation analysis, involving the relative probability of forming each reaction product, and, finally, dependences of Bremsstrahlung maximum energies on the yields for various types of the reactions were obtained, so that the more general applicability of photon-activation analysis to sensitive and accurate determination of many elements in a wide variety of materials can be considered.

EXPERIMENTAL

Accelerator

The 300-MeV linear electron accelerator of Tohoku University was used as the Bremsstrahlung source. The machine was operated with the "high current" accelerating section which provided a high intensity electron current, the peak current being at least 90 mA with energies up to 75 MeV. In many cases the pulse repetition rate was 200/sec with a pulse width of 3 μsec. The beam was deflected 90° from the original beam path of the accelerating section, and again deflected 45° onto the beam exit window. The spread of electron energies in this operating condition is 3% from the selected value. The electron beam produced Bremsstrahlung in a platinum converter with a thickness of 3 mm located 30 mm from the beam exit window. The average beam currents were measured at the position of the converter, by using a current monitor, and found, in typical operating conditions, to be 70 and 100 μA at 30 and 40–75 MeV, respectively.

Sample materials and irradiation

Samples of 52 elements, either in the form of metals or simple compounds, with chemical purity of 99·9% or better, were used. Metallic samples were small discs 6 mm in diameter with a thickness of about 0·1 mm. The powdered samples were individually wrapped in small pieces of aluminium foil and made into small discs 6 mm in diameter with a thickness of 2 mm. The amount loaded was between 10 and 100 mg, depending on the production rate of the desired activity. The sample was placed in a water-cooled sample holder on the Bremsstrahlung beam axis immediately behind the converter, for irradiation.

The distribution of the Bremsstrahlung flux behind the converter was far from homogeneous. In order to monitor the flux under such conditions, accurately weighed discs of copper, 0·1mm thick, were placed on the front and back of each sample and irradiated together with the sample. The ^{64}Cu activities produced by the ^{65}Cu(γ,n)^{64}Cu reaction were used for comparison. A mean specific activity was used for determining the dose rate of Bremsstrahlung to which the sample was exposed. The experimental results showed that the vertical spread of flux did not have a pronounced effect on the results, if the samples were limited to dimensions of the size given, and that the flux gradient along the length of the sample was less than 5%, even in the case of a sample of high atomic number. A typical irradiation was complete in 30–60 min.

Radioactivity measurement

The counting equipment consisted of a lithium-drifted germanium detector with a sensitive volume of 24 ml, ORTEC Model 8001–30, and its associated electronics, coupled to a TMC 1024-channel pulse-height analyser. The counting system had a resolution of 4 keV for the 661·6 keV gamma-line of ^{137}Cs. Energy calibration and photopeak counting efficiences were determined by counting a series of calibrated sources of known activities. The sample and copper monitor to be measured were separately sandwiched between 10-mm thick Lucite plates to absorb positrons from any positron emitters, and they were counted at a fixed position, 20 mm in most cases, from the active surface of the detector. Because of the high resolving power of the detector, no chemical separations were required for the present purposes, unless otherwise noted.

Nuclides were identified from a knowledge of the target nuclide, the gamma-ray spectra, decay data, data listed in the Table of Isotopes,[11] and current literature data. The initial decay rates of the various products were determined from decay curve analyses of the specified gamma-ray photopeak areas and normalizations were applied to them for the dose rate and sample weight.

Yield determination

The yield values were computed from the activity data by using the detection efficiency and the decay scheme parameters from the literature[11] for each nuclide. A yield was defined as the production rate of a nuclide due to a certain photonuclear reaction, in disintegrations/sec at the end of irradiation of one mole of a parent nucleus. This was converted into the corresponding saturation rate and expressed relative to that of the ^{65}Cu(γ,n)^{64}Cu process which occurred in the copper discs used for flux monitoring. In obtaining the yield data for 30-MeV Bremsstrahlung, a dose rate was determined by using the yield value of 2·8 × 10^{6}/mole/roentgen for the ^{63}Cu(γ,n)^{62}Cu reaction reported by Katz *et al.*,[12] and a yield was expressed in the form of dps/mole/R. In a typical operating condition at 30 MeV a dose rate of 4·41 × 10^{6} R/min was obtained at the sample position.

RESULTS AND DISCUSSION

Experimental sensitivity

Of the many product nuclides identified in this work, some 13 nuclides were selected for the sensitivity evaluations at two different Bremsstrahlung maximum energies, 30 and 60 MeV. The elements chosen for the sensitivity determinations were those having nuclear properties unfavourable for thermal-neutron activation analysis or those proved to be highly activated when irradiated with 20-MeV Bremsstrahlung.[2]

Table I lists the results. In Table I, all activity data have been expressed in counts/min/mg of the element at the end of 1 hr irradiation at each Bremsstrahlung maximum

TABLE I.—EXPERIMENTAL SENSITIVITIES FOR PHOTON ACTIVATION ANALYSIS WITH 30 AND 60 MeV BREMSSTRAHLUNG

Element	Reaction	Half-life of product	γ-ray energy, *MeV*	30 MeV		60 MeV	
				Photopeak activity,† *cpm/mg*	Limit of detection, μg	Photopeak activity, † *cpm/mg*	Limit of detection μg
C	^{12}C(γ,n)^{11}C	20·3 min	0·511*	4·44 × 10^{5}	0·23	2·71 × 10^{6}	0·037
O	^{16}O(γ,n)^{15}O	2·0 min	0·511*	7·78 × 10^{5}	0·13	5·32 × 10^{6}	0·019
F	^{19}F(γ,n)^{18}F	110 min	0·511*	2·94 × 10^{5}	0·034	6·43 × 10^{5}	0·016
Si	^{30}Si(γ,p)^{29}Al	6·56 min	1·28	3·68 × 10^{3}	27	1·10 × 10^{4}	9·1
Ti	^{46}Ti(γ,n)^{45}Ti	3·09 hr	0·511*	2·07 × 10^{4}	0·48	6·31 × 10^{4}	0·16
Fe	^{54}Fe(γ,n)^{53}Fe	8·9 min	0·511*	6·76 × 10^{4}	1·5	2·02 × 10^{5}	0·49
Ga	^{69}Ga(γ,n)^{68}Ga	68 min	0·511*	1·80 × 10^{6}	0·0056	2·45 × 10^{6}	0·0041
Sr	^{88}Sr(γ,n)^{87m}Sr	2·83 hr	0·388	4·95 × 10^{5}	0·020	8·19 × 10^{5}	0·012
Zr	^{90}Zr(γ,n)^{89m}Zr	4·18 min	0·588	5·31 × 10^{5}	0·19	1·21 × 10^{6}	0·083
Nb	^{93}Nb(γ,n)^{92m}Nb	10·16 d	0·934	1·51 × 10^{3}	6·6	2·75 × 10^{3}	3·6
Sn	^{124}Sn(γ,n)^{123m}Sn	40 min	0·160	4·86 × 10^{5}	0·21	7·09 × 10^{5}	0·14
Cs	^{133}Cs(γ,n)^{132}Cs	6·5 d	0·668	1·14 × 10^{4}	0·88	1·73 × 10^{4}	0·58
Pr	^{141}Pr(γ,n)^{140}Pr	3·4 min	0·511*	2·60 × 10^{6}	0·039	4·31 × 10^{6}	0·023

* Annihilation γ-rays.

† At the end of 1-hr irradiation with a standard dose rate of Bremsstrahlung photons. With this dose rate, 2·4 μCi of ^{64}Cu or 60·1 μCi of ^{62}Cu are produced in 1 mg of Cu at 30 MeV, or 4·7 μCi of ^{64}Cu per mg Cu at 60 MeV.

energy, when a standard amount of Bremsstrahlung photons had passed through the sample. With this dose rate, 2·4 μCi of ^{64}Cu were produced in 1 mg of copper with 30-MeV Bremsstrahlung, or 4·7 μCi with 60-MeV Bremsstrahlung.

The limit of detection was then calculated on the basis of minimum detectable photopeak area. The limit was assumed, depending on the half-life of the product in question, to be the quantity of the element needed to give either 100($t_{1/2} < 1$ hr) or 10 ($t_{1/2} > 1$ hr) cpm under the present experimental conditions. Sensitivities for light elements can be improved significantly by Bremsstrahlung irradiation with higher maximum energies. With our accelerator, most of the elements listed here can be detected in amounts well below 1 μg with 30-MeV Bremsstrahlung and these amounts are generally reduced by one-half with 60-MeV Bremsstrahlung. In practical analysis using non-destructive methods, however, these amounts should be altered, owing to difficulties in resolution of the complex spectra.

The yield as a function of atomic number

For most nuclei, an excitation energy of 30 MeV is sufficient to cause the emission of one or two particles, and, especially for heavy nuclei, of three particles. In this work, the yields for 138 different photonuclear reactions could be measured separately in 52 elements from carbon up to lead with 30-MeV Bremsstrahlung. These totalled 69(γ,n), 31(γ,p), 18(γ,2n), 13(γ,pn), 4(γ,α) and 3(γ,3n) reactions. Several of the (γ,γ') reaction products were also measured but are excluded from the present compilation because of their low production rates. The individual yield was plotted against the atomic number (Z) of the target element as shown in Fig. 1. The yield values for the (γ,n) reactions lie in the range 10^5–10^8/mole/R, and increase regularly with atomic number. The (γ,2n) yield values become important at around chromium and, rising rapidly with increasing atomic number, reach about 10% of those of the (γ,n) reactions with high-Z nuclei. The (γ,3n) reactions were only measured for the elements of high atomic numbers. For low-Z nuclides, the (γ,n) and (γ,p) yields are of the same order of magnitude. With increasing Z, however, the (γ,p) yield drops rapidly since proton emission is more and more hindered by the Coulomb barrier, It is seen that the (γ,p) yield curve levels off at a roughly constant value for elements with atomic number greater than 50. The presence of direct effects in the photoproton emission from heavier nuclei will be responsible for this behaviour as has been suggested by several workers.[13,14] The shape of the curve for the (γ,pn) reactions is very similar to that for the (γ,p) reactions, which shows an initial rise, reaches a maximum and then drops rapidly with increasing atomic number, with tailing around $Z = 60$.

For light elements both (γ,n) and (γ,p) reactions can be used for analytical purposes, whereas for heavier elements the (γ,n) reaction is the most widely used. Other types of reactions are generally of little practical use and are mainly considered only in interference studies.

Isotopic yield ratio

The cross-section for photoneutron emission from a neutron-excess isotope is expected to be large, and *vice versa* for photoproton emission. From the yield data obtained with 30-MeV Bremsstrahlung, several examples of this sort were selected and are listed in Table II. For the (γ,n) processes in antimony isotopes, the total cross-section for the formation of the excited state of ^{121}Sb is shared between two

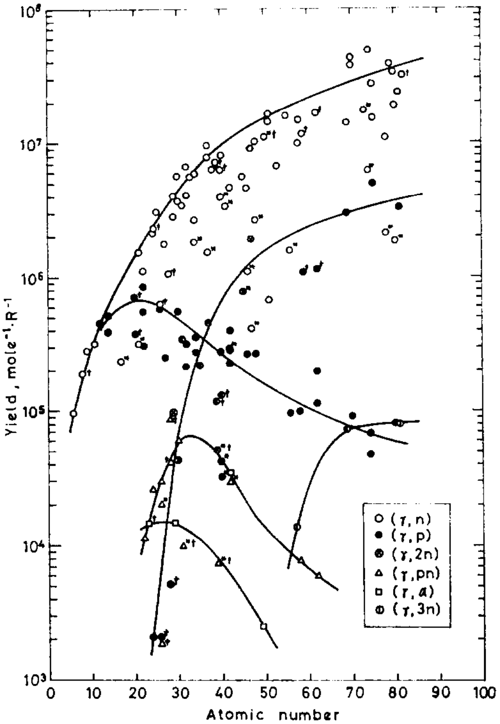


FIG. 1.—The yields of photonuclear reactions as a function of atomic number with 30-MeV Bremsstrahlung. *—The yields of metastable isomers, †—The yields for the reactions on target nuclides with "magic" neutron or proton numbers.

TABLE II.—THE YIELD RATIOS OF SEVERAL ISOTOPIC PAIRS WITH 30 MVe BREMSSTRAHLUNG

Reaction pathway	Isotopic pair	Yield ratio
Cu(γ,n)	^{64}Cu/^{62}Cu	1·72
Zn(γ,n)	^{65}Zn/^{63}Zn	1·62
Ge(γ,n)	^{75}Ge/^{69}Ge	1·71
Se(γ,n)	^{75}Se/^{73}Se	2·12
Sb(γ,n)	^{120}Sb/^{122}Sb/^{120}Sb (16 min) (5·8 d)	1/0·89/0·041
Ce(γ,n)	^{139}Ce/^{141}Ce	1·45
Yb(γ,n)	^{175}Yb/^{169}Yb	1·13
Si(γ,p)	^{28}Al/^{29}Al	1·30
Ti(γ,p)	^{46}Sc/^{47}Sc/^{48}Sc	1/0·67/0·39
Ge(γ,p)	^{72}Ga/^{73}Ga	1·52
Se(γ,p)	^{76}As/^{77}As	1·23
Mo(γ,p)	^{95}Nb/^{96}Nb/^{97}Nb	1/0·74/0·57
W(γ,p)	^{183}Ta/^{185}Ta	1·46

different ^{120}Sb isotopes, 16-min ^{120}Sb(1$^+$) and 5·8-d ^{120}Sb(8$^-$). The yield of the 5·8-d isotope was determined to be 4 % of that of the 16-min isotope as a result of the small probability of formation, owing to the large spin change.

As seen in Fig. 1, anomalously small yield values were obtained for the reactions on parent nuclides with "magic" neutron or proton numbers. These are the (γ,n) reactions on ^{16}O($Z = 8$), ^{52}Cr($N = 28$), ^{54}Fe($N = 28$), ^{58}Ni($Z = 28$), ^{89}Y($N = 50$), ^{90}Zr($N = 50$), ^{123m}Sn($Z = 50$), ^{141}Pr($N = 82$), ^{144}Sm($N = 82$) and ^{204}Pb($Z = 82$), the (γ,2n) reactions on ^{54}Fe, ^{59}Ni, ^{89}Y, ^{90}Zr, ^{141}Pr and ^{144}Sm, and the (γ,p) reactions on ^{43,44}Ca ($Z = 20$), the (γ,pn) reactions on ^{54}Fe, ^{58,60}Ni and ^{89}Y, and the (γ,α) reaction on ^{51}V($N = 28$).

Isomeric yield ratio

As seen in Fig. 1, the yields of metastable state isomers are low in general. The yield ratios of several isomeric pairs determined with 30-MeV Bremsstrahlung are given in Table III together with their spins and half-lives. The yield ratios favour those isomers having spin closer to that of the target nucleus, although the results for ^{89}Zr and ^{95}Nb isomers are exceptions. Similar results have been reported earlier.[15,16] Dependences of excitation energy on the isomeric yield ratios were not significant over the energy range investigated (see Fig. 3).

TABLE III.—THE YIELD RATIOS OF SEVERAL ISOMERIC PAIRS WITH 30 MeV BREMSSTRAHLUNG

Parent		Reaction	Residual					Yield ratio $\frac{Y_m}{(Y_m + Y_g)}$
Target nucleus	Spin			Ground state		Metastable state		
				Spin	Half-life	Spin	Half-life	
^{45}Sc	7/2$^-$	(γ,n)	^{44}Sc	2$^+$	3·92 hr	6$^+$	2·44 d	0·173
^{85}Rb	5/2$^-$	(γ,n)	^{84}Rb	2$^-$	33·0 d	6$^+$	20 min	0·147
^{90}Zr	0$^+$	(γ,n)	^{89}Zr	9/2$^+$	78·4 hr	1/2$^-$	4·18 min	0·381
^{107}Ag	1/2$^-$	(γ,n)	^{106}Ag	1$^+$	24 min	6$^+$	8·4 d	0·042
^{116}Cd	0$^+$	(γ,n)	^{115}Cd	1/2$^+$	53·5 hr	11/2$^-$	43 d	0·213
^{198}Pt	0$^+$	(γ,n)	^{197}Pt	1/2$^-$	18 hr	13/2$^+$	80 min	0·166
^{198}Hg	0$^+$	(γ,n)	^{197}Hg	1/2$^-$	65 hr	13/2$^+$	24 hr	0·089
^{89}Y	1/2$^-$	(γ,2n)	^{87}Y	1/2$^-$	80 hr	9/2$^+$	14 hr	0·304
^{96}Mo	0$^+$	(γ,p)	^{95}Nb	9/2$^+$	35 d	1/2$^-$	90 hr	0·430
^{54}Fe	0$^+$	(γ,pn)	^{52}Mn	6$^+$	5·7 d	2$^+$	21 min	9·79

The yield as a function of excitation energy

Reactions of the type (γ,xn). For most of the medium and heavy weight nuclei, the energy range of 30-MeV bremsstrahlung covers a substantial part of the excitation function of the (γ,n) reaction, and hence the yield reaches an almost constant value beyond 30 MeV. Typical yield curves for the (γ,n) reactions are given in Fig. 2. The yield curve for the ^{12}C(γ,n)^{11}C reaction ($-Q = 18{\cdot}72$ MeV), however, rises at 60 MeV to a value three times higher than that at 30 MeV.

The yield of a reaction with the emission of more than one neutron appears to be strongly energy-dependent. Several yield curves for the types (γ,2n), (γ,3n) and (γ,4n) are shown in Fig. 3. The relative yields of forming each nuclide by the (γ,xn) reactions appear likely to show almost an order of magnitude decrease with each unit increasing in x. Figure 4 gives the relative yields for the (γ,xn) reactions on ^{89}Y and ^{169}Tm.

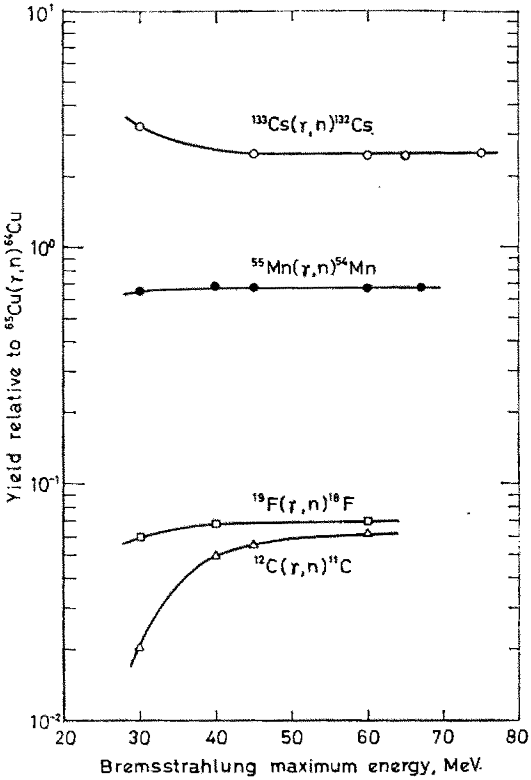


FIG. 2.—The yield curves for several (γ,n) reactions.

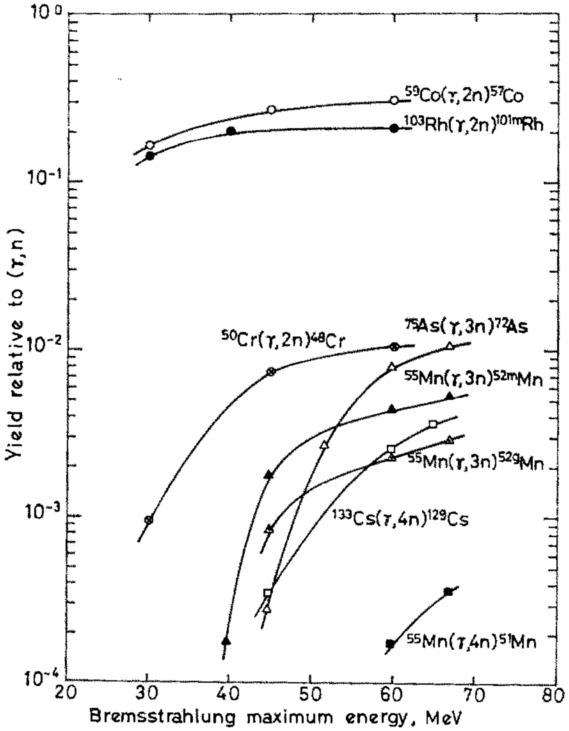


FIG. 3.—The yield curves for several (γ,2n), (γ,3n) and (γ,4n) reactions.

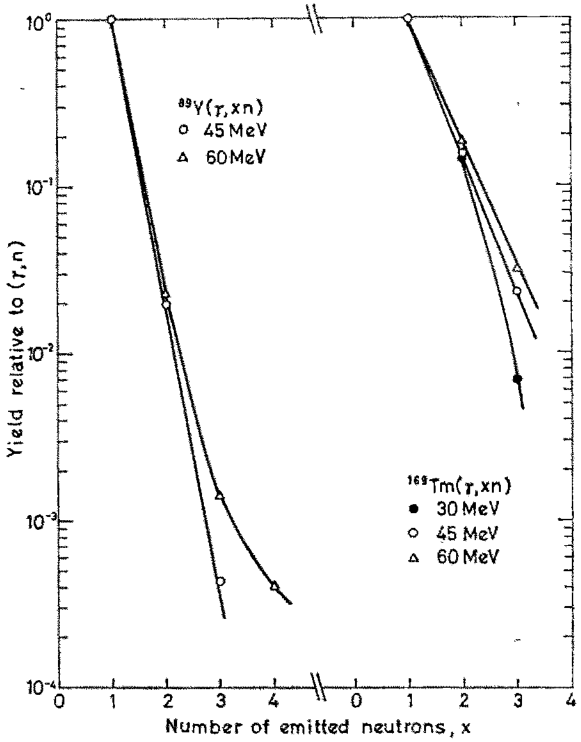


FIG. 4.—The relative yields of the (γ, xn) reactions on ^{89}Y and ^{169}Tm as functions of x.

Reactions of the type (γ,pxn). The yield curves for the (γ,p) reactions on ^{44}Ca, ^{96}Mo and ^{152}Sm are shown in Fig. 5. Over the energy range investigated, the yield increases gradually with increasing energy. The contribution of the direct photoproton emission mechanism will become more inportant at high energies, thereby causing the enhancement of the yield values. The enhancement of the yield values is more significant for the (γ,pn), (γ,p2n) and (γ,p3n) reactions as shown in Fig. 6. For the production of reactions of such types, the quasi-deuteron effect plays an important role, depending on the atomic number of the reacting nucleus and on the incident photon energy.[17] At high energies this process can be responsible for the increase in the yield values.

Other complex reactions. Other reactions with the emission of more particles are substantially forbidden from mass-threshold considerations for most of the light nuclei in the energy range covered in this experiment, but in some heavy nuclei they can still occur.

When iodine activities were chemically separated from an irradiated caesium sample, the ^{126}I activity formed by the (γ,2p5n) reaction on ^{133}Cs ($-Q = 55{\cdot}4$ MeV) was measured together with the ^{131}I and ^{130}I activities. The yields of these reactions are given as a function of Bremsstrahlung maxium energy in Fig. 7. The reaction paths other than (γ,2p5n) would also occur simultaneously; the reactions (γ,α3n) ($-Q = 27{\cdot}1$ MeV), (γ,dt2n) ($-Q = 44{\cdot}7$ MeV), (γ,^{3}He4n) ($-Q = 47{\cdot}7$ MeV), (γ,2d3n) ($-Q = 51{\cdot}0$ MeV) and (γ,pd4n) ($-Q = 53{\cdot}2$ MeV).

Although the yield values for such types of reactions are very small, a difficult

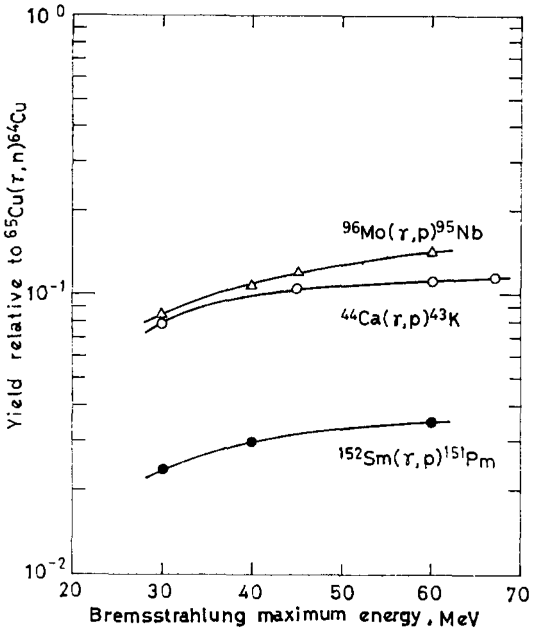


FIG. 5.—The yield curves for several (γ,p) reactions.

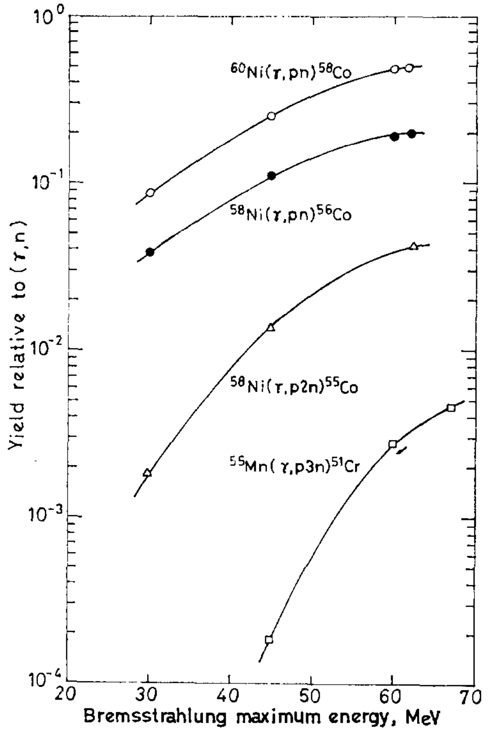


FIG. 6.—The yield curves for several (γ,pn), (γ,p2n) and (γ,p3n) reactions.

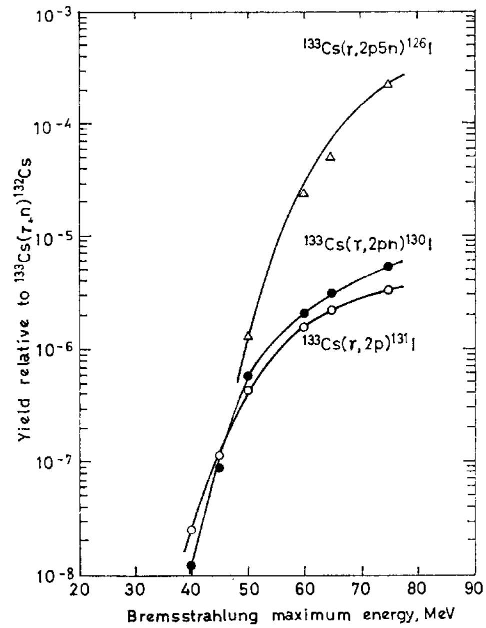


FIG. 7.—The yield of the ^{133}Cs(γ,2pxn) reactions as a function of Bremsstrahlung maximum energy.

interference problem will occur when these reactions produce a nuclide identical to that in the activation analysis.

CONCLUSION

Although considerable effort has been devoted to photon-activation analysis for traces of light elements, it appears to be quite promising to apply this method to the determination of many other elements at trace levels. Under the present experimental conditions with our accelerator, sensitivities well below 1 μg were obtained for many elements. These sensitivities would be improved with an accelerator giving Bremsstrahlung of a much higher dose rate, and with better counting efficiencies. The amount of activation is very dependent on electron energy, and the (γ,2n) reactions, besides the (γ,n) and (γ,p) reactions, become useful in analysis. The interference problem, however, becomes serious under such conditions, but the yield data for various photonuclear reactions which occur simultaneously at a given electron energy should serve as a useful guide. The combination of an efficient chemical separation and solid-state detection technique will also improve sensitivity, accuracy and versatility in the determination of the heavier elements in photon activation analysis.

Acknowledgment—The authors express their appreciation to members of the Institute of Nuclear Science, Tohoku University, for their very fine service with the irradiations.

Zusammenfassung—Experimentelle Reaktionsausbeuten wurden für verschiedene Typen von Kern-Photoreaktionen ermittelt. Sie wurden in 52 Elementen durch Bestrahlung mit Bremsstrahlung (Maximalenergien zwischen 30 und 72 MeV) ausgelöst und die entstandenen Aktivitäten mit einem Lithium-gedrifteten Germaniumdetektor nachgewiesen. Aus den Ergebnissen wurden Empfindlichkeiten der Photoaktivierungsanalyse berechnet; die Reaktionsfähigkeit von hochenergetischen Photonen mit Kernen in einem weiten Bereich von Ordnungszahlen wird diskutiert. Einige kernchemische Überlegungen, etwa die relative Wahrscheinlichkeit der Bildung eines bestimmten Produkts als Folge der ($\gamma, xnyp$)-Reaktionen, werden ebenfalls mitgeteilt.

Résumé—On a déterminé les rendements de réaction expérimentaux pour divers types de réactions photonucléaires, induites dans 52 éléments au moyen d'irradiation "Bremsstrahlung" avec énergies maximales allant de 30 à 72 MeV, et détection des activités résultantes par un détecteur au germanium modifié au lithium. Des résultats obtenus, on a évalué les sensibilités en analyse par activation de photons et l'on discute de la réactivité des photons de haute énergie avec les noyaux dans un large domaine de nombres atomiques. On présente aussi quelques considérations nucléaires en analyse par activation de photons, comprenant la probabilité relative de formation de chaque produit comme résultat des réactions (γ, $xnyp$).

REFERENCES

1. E. Schweikert and Ph. Albert, *Colloque Sur les Methodes Radiochimiques d'Analyse*, Salzburg, I.A.E.A., SM-SS/66, 1964.
2. Y. Oka, T. Kato, K. Nomura and T. Saito, *J. Nucl. Sci. Technol.*, 1967, **4**, 345.
3. G. H. Anderson, F. M. Graber, V. P. Guinn, H. R. Lukens and D. M. Settle, *Proc. Symp. Nuclear Activation Techniques in Life Sciences*, Amsterdam, I.A.E.A., SM-91/63, 1967.
4. D. Brune, *Anal. Chim. Acta*, 1969, **44**, 9.
5. G. J. Lutz, *Anal. Chem.*, 1969, **41**, 424.
6. Ch. Engelmann, *J. Radioanal. Chem.*, 1970, **6**, 399.
7. Y. Oka, T. Kato, K. Nomura and T. Saito, *Bull. Chem. Soc. Japan*, 1967, **40**, 575.
8. Y. Oka, T. Kato, K. Nomura, T. Saito and H.-T. Tasi, *ibid.*, 1968, **41**, 380.
9. *Idem*, *ibid.*, 1968, **41**, 2660.
10. Ch. Engelmann, *Nucl. Instr. Methods*, 1971, **93**, 197.
11. C. M. Lederer, J. M. Hollander and I. Perlman, *Table of Isotopes*, 6th Ed., Wiley, New York, 1967.
12. L. Katz and A. G. W. Cameron, *Can. J. Phys.*, 1951, **29**, 518.
13. E. V. Weinstock and J. Halpern, *Phys. Rev.*, 1954, **94**, 1651.
14. V. G. Shevchenko and B. A. Yuryev, *ibid.*, 1962, **37**, 495.
15. Y. Oka, T. Kato and A. Yamadera, *Bull. Chem. Soc. Japan*, 1968, **41**, 1606.
16. T. Kato and A. F. Voigt, *J. Radioanal. Chem.*, 1970, **4**, 325.
17. J. S. Levinger, *Phys. Rev.*, 1951, **84**, 43.

Talanta, 1972, Vol. 19, pp. 527 to 537. Pergamon Press. Printed in Northern Ireland

SOLID-LIQUID EXTRACTION AS A PRECONCENTRATION TECHNIQUE IN TRACE ELEMENT ANALYSIS

EXTRACTION OF TRACE IMPURITIES FROM METAL CHLORIDES

ATSUSHI MIZUIKE®, KATSUAKI FUKUDA and YOJI OCHIAI
Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received* 14 *June* 1971. *Accepted* 29 *August* 1971)

Summary—Microgram quantities of iron, cobalt, copper, zinc and cadmium are extracted with various aqueous, organic and mixed solvents from chlorides of sodium, potassium, nickel, cadmium, barium and lead prepared by evaporation of aqueous sample solutions. An ultrasonic field accelerates the extraction, and satisfactory trace recoveries and separation factors are achieved in several systems within a reasonable time. The application to a polarographic determination and a two-stage separation technique are also described.

VARIOUS methods of separation have been applied to the preconcentration of trace elements from matrix elements before the trace determination, to make the sensitivity, precision and accuracy better than those which direct determination would achieve.[1,2] The most commonly used methods include volatilization, liquid-liquid extraction, precipitation, electrodeposition and ion-exchange. Solid-liquid extraction of trace elements from solids, with appropriate solvents, can also be employed for the same purpose, but very few applications have been made to date. Rynasiewicz *et al.*[3] extracted traces of boron from solid sodium chloride with 95% ethanol for the photometric determination of boron in sodium metal. Morrison and Rupp[4] employed the solid-liquid extraction of traces of boron from crystalline silicic acid with water, as a preconcentration technique in the emission spectrographic determination of boron at the parts per milliard level (ppM) in silicon. The same preconcentration technique was also applied to the determination by the isotope-dilution method with a mass spectrometer.[5] In this laboratory, the extraction of nanogram or microgram quantities of iron, cobalt, copper and zinc from solid basic bismuth nitrate with 0·07M phosphoric acid-0·12M hydrochloric acid or water was studied and applied in the square-wave polarographic or the emission spectrographic determination of these impurity elements in high-purity bismuth and reagent-grade bismuth nitrate pentahydrate.[6-8] Because very little information has hitherto been available on this subject, more work should be done to evaluate solid-liquid extraction as a preconcentration technique in trace element analysis in the light of criteria such as trace recoveries, separation factors,* contamination hazards, simplicity, rapidity and cost. The present paper reports the extraction of microgram quantities of impurity elements from several solid metal chlorides, with various solvents.

---

* The separation factor S for a matrix element M with respect to a desired trace element T is defined as follows:

$$S = (Q_M/Q_T)/(Q_M^0/Q_T^0)$$

where Q_T^0 = the quantity of T in the sample; Q_M^0 = the quantity of M in the sample; Q_T = the quantity of T after the separation; Q_M = the quantity of M after the separation.

EXPERIMENTAL

Apparatus

A Fujitsu NaI(Tl) well-type scintillation counter (44 × 50 mm). A Yanaco PF-501 polarograph. A Hirama model VI spectrophotometer with matched 20-mm cells. A Kaijo Denki model 4335 ultrasonic generator (29 kHz, 150 W).

Reagents

Tracer solutions. Hydrochloric acid solutions (0·1 *M*) containing 1 μg/ml of ^{59}Fe-labelled Fe(III), ^{60}Co-labelled Co(II), ^{64}Cu-labelled Cu(II), ^{65}Zn-labelled Zn(II), ^{110m}Ag-labelled Ag(I) and 10 μg/ml of ^{115}Cd-labelled Cd(II).

Matrix solutions. NaCl, KCl, $NiCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2{\cdot}5H_2O$, $BaCl_2 \cdot 2H_2O$ and $Pb(NO_3)_2$ dissolved in water (0·1 or 0·2 g of the matrix metal elements per ml).

Water was purified by distillation and ion-exchange. All the reagents used were of reagent grade and were used without further purification.

Standard procedure

Place 5 or 10 ml of matrix solution (containing 1 g of the matrix element) and 1 ml of tracer solution in a 50-ml beaker. In case of the lead matrix, add 4 ml of 12*M* hydrochloric acid. Evaporate the solution to dryness on a water-bath and then on an electric hot-plate at ca. 130°, rotating the beaker rapidly to prevent loss by spattering. Add 2 ml of water, stir, and evaporate again to dryness as described above. Cool to room temperature, and triturate the residue with a glass rod. Transfer the triturate to a 50-ml glass-stoppered Erlenmeyer flask. Rinse the beaker with 20 ml (or 40 ml for the cadmium matrix) of a solvent, and add the washings to the flask. Fasten the stopper, suspend the flask by a string in a 35-litre tank containing water and a transducer, and apply ultrasonics for 30 min (or 5 min for the lead matrix) to effect vigorous stirring. Transfer the contents of the flask quantitatively to a 50-ml round-bottomed centrifuge tube, and centrifuge for 3 min (or 6 min for the cadmium matrix) at 4000 rpm. Transfer the supernatant liquid into a second 50-ml beaker. Rinse the flask with 5 ml (or 10 ml for the cadmium matrix) of the solvent, and add the washings to the centrifuge tube. Immerse the tube in the tank, and apply ultrasonics for 30 sec while stirring with a glass rod. Centrifuge for 3 min (or 6 min for the cadmium matrix). Transfer the supernatant liquid to the beaker containing the first extract. If the combined liquid is turbid, filter it through a Millipore filter (Polyvic BS, mean pore size 2·0 μm, diam. 25 mm) or a glass fibre filter (Toyo Roshi, diam. 25 mm; for solvents containing acetone). Dilute the liquid to 25 ml (or 50 ml for the cadmium matrix) with the solvent in a volumetric flask, and measure the gamma-activity of a 2-ml aliquot to obtain the trace recovery.

Determine the matrix element dissolved in the solvent by the following methods after evaporation of the solvent; gravimetry for sodium, potassium and lead, polarography for lead and cadmium, EDTA titration for cadmium and barium, and spectrophotometry for nickel.

RESULTS

Effect of extraction time and ultrasonics on the extraction

Typical results are shown in Fig. 1. The application of a sound field accelerates the extraction of trace elements as well as dissolution of the matrix element, and the apparent equilibrium is achieved in about 30 min. The solvent is saturated with the matrix element before the trace recoveries reach their maxima. The same results were also obtained in the extractions of zinc from sodium chloride and barium chloride with a 1:1 n-butanol–12*M* hydrochloric acid mixture and from cadmium chloride with a 999:1 acetone–12*M* hydrochloric acid mixture. However, the extraction of iron and zinc from lead chloride with a 999:1 ethanol–12*M* hydrochloric acid mixture was completed within 5 min.

Table I lists the change in particle size during the extraction in a sound field. Without a sound field, much larger particles remained after the extraction. Although pulverization by ultrasonics is very effective, a preliminary crushing with a glass rod is essential to obtain a sufficiently small particle size after the extraction for a perfect trace recovery, especially in the extraction from sodium chloride, as shown in Table II.

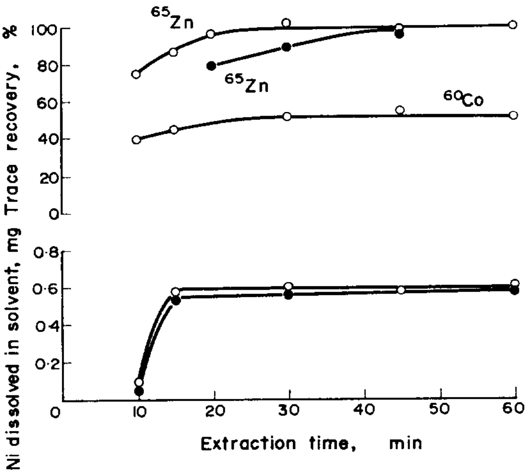


Fig. 1.—Extraction of cobalt and zinc from nickel chloride. 1 g of Ni + 1 μg of labelled Co or Zn; 25 ml of acetone–12*M* HCl (99:1). ○ with sound field ● with mechanical stirring.

Table I.—Pulverization of solids during extraction in a sound field

Matrix element (1 g)	Solvent	Particle size,* *μm*, after extraction for			
		0 min	3 min	10 min	30 min
Na	n-butanol–12*M* HCl (1:1), 25 ml	40–150	40–100	20–60	10–20
Ni	acetone–12*M* HCl (99:1), 25 ml	—	~20	~5	~1
Cd	acetone–12*M* HCl (999:1), 50 ml	100–200	600†	40–100	~2
Ba	n-butanol–12*M* HCl (1:1), 25 ml	30–150	~60	~10	~2

* Microscopic measurement.
† Increase due to swelling.

Table II.—Effect of particle size of sodium chloride on zinc recovery

Crushing with a glass rod	Size distribution of NaCl before extraction, % *w/w*					^{65}Zn recovered, %
	<60 mesh	60–100 mesh	100–150 mesh	150–200 mesh	>200 mesh	
Rough	27, 34	23, 17	12, 16	17, 18	21, 15	80, 69
Extensive	5, 3	16, 13	22, 25	25, 19	32, 40	96, 98

Conditions: 1 g of Na + 1 μg of labelled Zn; 25 ml of n-butanol–12*M* HCl(1:1); 30 min extraction.

These large particles are generally agglomerates of crystals, but a minor agglomeration occurs in the case of lead chloride crystals (60–100 μm in size), which remain nearly unchanged during the extraction.

Extraction by the standard procedure

Table III summarizes the solid–liquid extraction of trace elements from several metal chlorides with various solvents by the standard procedure described previously,

TABLE III.—SOLID–LIQUID EXTRACTION OF TRACE ELEMENTS FROM METAL CHLORIDES

Matrix* element (1 g)	Solvent (25 ml)	Trace recovery, %					Matrix element dissolved in solvent, *mg*
		Fe	Co	Cu	Zn	Others	
Na	12*M* HCl	95	93	96	96, 98	Ag 0, 1	16
	ethanol	96	95	94	96	Ag 2, 3	6·8
	n-butanol	78, 82	80, 86	78	80, 84	Ag 0	0·4
	n-butanol–12*M* HCl (99:1)	86, 88	88, 90	86	93, 94		1·6
	n-butanol–12*M* HCl (9:1)	89, 91	91, 94	89	97, 99		3·2
	n-butanol–12*M* HCl (3:1)	93, 94	92, 94	94	96, 98		7·2
	n-butanol–12*M* HCl (1:1)	96, 96, 97	94, 95, 97	95, 97	95, 96, 98		10
	acetone	96	93	97	95		8.4
	acetone–12*M* HCl (99:1)	95	96	94	95		24
K	12*M* HCl	98, 99	96, 100	96	99, 100		219
	ethanol	95, 95	92, 93, 95	94	95, 97, 97		5·5
	n-butanol	83, 87	70, 74	83	71, 79		0.5
	n-butanol–12*M* HCl (99:1)	93, 95	87, 91	93	95, 97		1·5
	n-butanol–12*M* HCl (9:1)	95, 97	92, 94, 95	97	97, 97, 100		3·5
	n-butanol–12*M* HCl (3:1)	96,98	95, 96	96	96, 98		13
	n-butanol–12*M* HCl (1:1)	96, 99	97, 99	95	98, 98	Ag 10, 13	113
	acetone	95	98	94	96		2·5
	acetone–12*M* HCl (99:1)	95	98	95	97		21
Ni	12*M* HCl	98, 98	97	96	100, 101		58
	acetone	21	8	22	37		0·010
	acetone–12*M* HCl (999:1)	37	28	38	62		0·035
	acetone–12*M* HCl (99:1)	96	52, 54	95	103		0·60
	acetone–12*M* HCl (9:1)	96, 99	96, 98, 98	98	97, 100	Ag 7	5

Cd†	acetone	12	28	17	31	Ag 1	1·5
	acetone–12*M* HCl (999:1)	97	96	99	97, 98, 100	Ag 0	10
	acetone–12*M* HCl (99:1)	98, 101	97, 99		99		54
	acetylacetone	10	32		22	Ag 1	2·0
	acetylacetone–12*M* HCl (999:1)	96	95	97	93	Ag 2	26
	dioxane	23	35		21		0·036
	dioxane–12*M* HCl (99:1)	20	35		31		0·060
Ba	12*M* HCl	96, 100	97	93	98, 100		1·3
	n-butanol	75, 79	46	60	68, 73		0·38
	n-butanol–12*M* HCl (99:1)	78, 84	54	72	77, 83		
	n-butanol–12*M* HCl (9:1)	85, 88	67	85	85, 89		0·51
	n-butanol–12*M* HCl (3:1)	92	90, 94	90	92, 94		0·74
	n-butanol–12*M* HCl (1:1)	97, 99, 100	95	92	98, 100	Ag 1, 2	0·96
	acetone	14	18	18	26, 30		0·028
	acetone–12*M* HCl (999:1)	13, 17	20, 24	17	33		0·035
	acetone–12*M* HCl (99:1)	40	35	48	49, 58		0·10
Pb‡	water	79			97		200
	1·2*M* HCl	96, 97	98		99		50
	ethanol	13, 17		22	35, 40		
	ethanol–12*M* HCl (999:1)	99, 100, 103	96, 98, 99	98	97, 97, 100	Ag 2, 4. Cd 98, 100	0·059, 0·072
	ethanol–12*M* HCl (99:1)	98	100		97		0·69
	acetone			20	27, 33		
	acetone–12*M* HCl (999:1)			97	95		0·29

30 min extraction

* 1 or 10 μg of labelled trace element added.

† 50 ml of solvent.

‡ 5 min extraction.

which was established on the basis of the experimental results above. Trace recovery is always quite reproducible at greater than 90% yields. Negligible amounts of nitrate and free acids were found in solid lead chloride prepared by the standard procedure. Loss of trace elements due to adsorption or adhesion on the walls of the 50-ml beaker used for evaporation of sample solutions was always less than 1%. Fifty ml of solvent was employed for the cadmium matrix, because cadmium chloride swells in acetone and acetylacetone, forming voluminous addition compounds, which makes the extraction difficult with only 25 ml of solvent. Filtration of the extracts was necessary in the extractions from lead chloride with water, and from barium chloride with solvents containing n-butanol (sometimes with solvents containing acetone).

Effect of matrix quantity on the extraction

Table IV shows that trace recoveries decrease with increase of the quantity of matrix elements in extractions with a fixed amount of solvent. Because stirring due to a sound field was insufficient when larger quantities of solids were used, mechanical stirring was used simultaneously. Nevertheless, trace recoveries were poor for more than 3 g of matrix elements.

TABLE IV.—EFFECT OF QUANTITY OF MATRIX ELEMENT ON TRACE RECOVERY

Matrix element taken, *g*		Trace element added (1 μg)	Trace recovery, %	
			With sound field	With sound field and mechanical stirring
K	1	Fe	95, 97	96
	2	Fe	86	97
	3	Fe	64	83
	5	Fe	48	—
Ba	1	Zn	98, 100	—
	2	Zn	81, 85	94
	3	Zn	72	92
	5	Zn	61	80, 82

Solvent 25 ml of n-butanol–12*M* HCl (9:1) for K, 25 ml of n-butanol–12*M* HCl (1:1) for Ba; 30 min extraction.

Repeated extractions

Extraction of traces of cobalt from nickel chloride with a 99:1 acetone–12*M* hydrochloric acid mixture was incomplete (Fig. 1 and Table III). Therefore, repeated extractions with portions of fresh solvent were carried out, with the results given in Table V. The cobalt recovery is directly proportional to the amount of nickel dissolved, up to the 5th extraction, and nearly perfect recovery is attained by the use of about 50 ml of the solvent.

Effect of water in organic solvents on the extraction

Organic solvents such as ethanol and acetone usually contain small amounts of water, and also absorb water from air. For example, in this study the ethanol contained 0·2% w/w of water and absorbed about 0·3% w/w of water during the extraction procedure, and the acetone contained 0·5% w/w of water (Karl Fischer

TABLE V.—REPEATED EXTRACTIONS OF COBALT FROM NICKEL CHLORIDE* WITH A 99:1 ACETONE–12*M* HYDROCHLORIC ACID MIXTURE

No. of extraction†	Volume of solvent, *ml*	^{60}Co recovered, %	Ni dissolved in solvent, *mg*
1	20	42	0·47
2	10	24	0·23
3	5	9	0·11
4	5	10	0·12
5	5	7	0·10
6	5	4	0·12
7	5	1	0·09
	Total 55	97	1·24

* 1 g of Ni + 1 μg of labelled Co.
† 20 min each.

TABLE VI.—EFFECT OF WATER IN SOLVENT ON EXTRACTION OF ZINC

Matrix element*	Solvent	Water in organic solvent, % *w/w*	^{65}Zn recovered, %	Matrix element dissolved in solvent, *mg*
Cd, 1 g	acetone–12*M* HCl	0·5	98	10
	(999:1), 50 ml	1·5	98	15
		5·5	96	38
Pb, 1 g	ethanol–12*M* HCl	0·2	98	0·059, 0·072
	(999:1), 25 ml	0·7	100	0·061
		1·2	98	0·057
		5·2	100	0·10

* 1 μg of labelled Zn added.

determination). Table VI shows the effect of water in organic solvents on the extraction of zinc.

DISCUSSION

In Fig. 2 are plotted the curves for recovery of a particular trace element as a function of the quantity of matrix element dissolved, from the data given in Table III. In each case, the points obviously fell on one universal curve irrespective of the solvents used. Also, the curves resemble each other for iron, cobalt, copper and zinc in any matrix except for nickel.

The results shown in Fig. 2 and Tables IV and V suggest that the following inequality must be satisfied for nearly perfect trace recoveries within 30 min of extraction:

$$\Delta m/m > k \tag{1}$$

where Δm is the quantity of the matrix element dissolved in the solvent, m the total amount of the matrix element, and k a constant independent of the quantity of the matrix element and the kind and quantity of the solvent, provided that the state of the solid phase is invariant.

We infer the following mechanism for the present solid–liquid extraction systems from the experimental results described previously. After evaporation of the sample solution, trace elements are present on the surfaces of crystals (or their agglomerates)

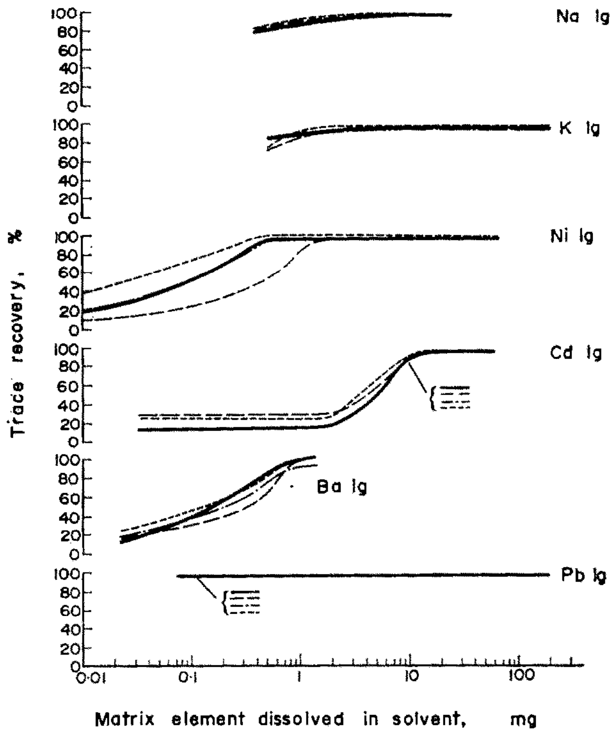


FIG. 2.—Relationship between quantity of matrix element dissolved in solvent and trace recovery.
Fe (—), Co (— —), Cu (— — — —), Zn (- - -), 1 μg added; 25 ml of solvent, except for Cd (50 ml); 30 min extraction, except for Pb (5 min).

of pure chlorides of the matrix element (anhydrous, for sodium, potassium and lead; hydrated, for nickel, cadmium and barium), or in the interstitial space in the agglomerates. During the extraction in a sound field, the agglomerates are pulverized, and the trace elements are brought into good contact with the solvent and dissolved together with part of the matrix.

Extremely low recoveries of silver are presumably due to its adsorption on the solid phase during the evaporation or the extraction step. The adsorption during the latter step was proved by a separate adsorption experiment, in which about 80% of silver was adsorbed on solid lead chloride from a mixed solution of 1 ml of tracer solution (^{110m}Ag) and 24 ml of a 999:1 ethanol–12*M* hydrochloric acid mixture within 10 min of ultrasonic irradiation. Similarly, adsorption of copper on barium chloride from acetone and of iron on lead chloride from ethanol was observed. Therefore, low recoveries of iron and copper in the extraction with pure organic solvents or water might be partly ascribed to adsorption on the solid phase. Formation of mixed crystals of matrix and trace elements during the evaporation and recrystallization during the extraction appear to be negligible in the present extraction systems. To explain the discrepancies among curves in Fig. 2, especially for nickel chloride, more detailed investigations on the formation of the solid phase, adsorption phenomena, and various factors affecting the constant *k* would be necessary.

The following suggestions will be useful as a guide for designing solid–liquid extraction methods for trace element analysis.

(1) Prepare larger crystals to make k smaller.
(2) Select the solvent and its quantity so that $\Delta m/m$ is a little larger than k. Also, consider adsorption of trace elements on the solid phase and ease in stripping for the subsequent determination or separation step.
(3) Apply ultrasonics during the extraction.
(4) If the separation factors for matrix elements with respect to desired trace elements are insufficient, use the two-stage separation technique described later.

At present, it is difficult to evaluate fully solid–liquid extraction as a preconcentration technique in trace element analysis. However, by choosing favourable solid phases, solvents and manipulations, quite satisfactory trace recoveries and separation factors may be easily obtained by this technique. Precipitation of 1 g of barium or lead as chloride from 25 ml of aqueous sample solution is also applicable to the preconcentration of impurity elements such as zinc at the microgram level. After the precipitation, 95–97% of zinc remains in the supernatant solution with 2 mg of barium or 40 mg of lead. These results are inferior to those obtained by the present technique (see Table III).

APPLICATIONS

Determination of impurities in lead

The proposed preconcentration technique was successfully applied in the square-wave polarographic determination of ppM levels of zinc and cadmium in high-purity lead and reagent-grade lead nitrate.

Recommended procedure. Transfer 2·5 g of lead to a 50-ml beaker, add 15 ml of 7*M* nitric acid, cover with a watch-glass, and heat gently to dissolve. Evaporate the solution to dryness, and then dissolve the residue in 15 ml of water. (For lead nitrate, dissolve 4 g of sample in 15 ml of water.) Dilute the solution to 25 ml with water in a volumetric flask. Place a 5- or 10-ml aliquot in another 50-ml beaker and add 4 ml of 12*M* hydrochloric acid. Evaporate the solution to dryness, and extract zinc and cadmium from the residue with a 999:1 ethanol–12*M* hydrochloric acid mixture, as described under *Standard procedure*. Filter the extract through a Millipore filter, and evaporate to near dryness in a 50-ml fused silica beaker on a water-bath. Add 1 ml of 60% perchloric acid, and evaporate to dryness. Dissolve the residue in 1 ml of 5*M* phosphoric acid, and dilute to 5 ml with water. Transfer the solution to a polarographic cell, deaerate with nitrogen for 5 min, and record the square-wave polarogram from −0·8 to −1·5 V *vs.* the mercury pool.

The calibration curve was linear up to at least 2 μg of zinc or cadmium with a maximum deviation of 0·02 μg. No interference results from the presence of 150 μg of lead(II), and 10 μg each of iron(III), cobalt(II), nickel(II), antimony(III, V), arsenic(III, V), tin(IV) and bismuth(III) in the determination of 0·2 μg of zinc or cadmium. Analytical results are given in Table VII. The blank values for the entire procedure were 0·05 μg of zinc and 0·00 μg of cadmium. A determination requires about 2 hr.

Two-stage separations

According to inequality (1), the total amount of a matrix element (m) must be reduced to minimize the amount of it dissolving in a solvent (Δm), if k is constant. Therefore, two-stage separation appears to be a promising means of improving the

TABLE VII.—POLAROGRAPHIC DETERMINATION OF IMPURITIES IN LEAD

Sample	Aliquot taken	Found, *ppm* Zn	Found, *ppm* Cd
Reagent-grade lead nitrate, 4·00 g	$\frac{1}{5}$	0·38	0·09
	$\frac{2}{5}$	0·37	0·07
	$\frac{2}{5}$*	0·34	0·08
		Av. 0·36	0·08
99·999% lead metal, 2·50 g	$\frac{1}{5}$	0·35	0·12
	$\frac{2}{5}$	0·38	0·13
	$\frac{2}{5}$*	0·36	0·13
		Av. 0·36	0·13

* 1 μg of Zn and 0·1 μg of Cd added before extraction.

separation factors for the matrix element with respect to the trace elements of interest. In this technique, after the first solid–liquid extraction, the solvent is stripped by evaporation, and then the second extraction is carried out on the residue with another solvent. For the selection of the solvent used in the first extraction, perfect trace recoveries and ease in evaporation are prime considerations.

Procedure. Evaporate to dryness 5–10 ml of a sample solution containing 1 g of matrix element and 1 μg of labelled zinc, and extract zinc from the residue with 5 ml of a solvent in a test-tube (14 mm bore, 80 mm long, with a silicone rubber stopper) for 20 min in a sound field, as described under *Standard procedure*. Centrifuge for 5 min, using the same test-tube. Transfer the supernatant liquid to another test-tube. Wash the residue in the first test-tube twice with 3 and then 2 ml of the solvent, with the aid of a centrifuge, and add the washings to the extract in the second test-tube. Evaporate the solution to dryness on a water-bath and then heat the residue in an air-oven at about 110° for 10 min. Cool, and triturate the residue with a glass rod. Add 4 ml of another kind of solvent, and extract zinc from the residue for 30 min in a sound field. Centrifuge for 3 min. Transfer the supernatant liquid to a 10-ml volumetric flask. Add 1 ml of the second solvent to the second test-tube, and apply ultrasonics for 30 sec. Centrifuge, and transfer the supernatant liquid to the volumetric flask. Dilute to the mark with the second solvent, and measure the gamma-activity of a 1-ml aliquot. Determine the matrix element dissolved in the solvent, as described previously.

The results are summarized in Table VIII. The separation factors were improved by a factor of 5–10 as compared with those obtained by the standard procedure with

TABLE VIII.—TWO-STAGE SEPARATIONS

	1st extraction		2nd extraction		
Matrix element* (1 g)	Solvent (10 ml)	Matrix element dissolved, *mg*	Solvent (5 ml)	^{65}Zn recovered, %	Matrix element dissolved, *mg*
K	ethanol–12*M* HCl (99:1)	8	n-butanol–12*M* HCl (9:1)	97	0·8
Ni	acetone–12*M* HCl (9:1)	1·5	acetone–12*M* HCl (99:1)	96	0·095
Cd	ethanol–12*M* HCl (999:1)	75	acetone–12*M* HCl (999:1)	95	0·93

* 1 μg of labelled Zn added.

the second solvent (*cf.* Table III). More improvement may be achieved by choosing more suitable conditions.

Acknowledgement—We would like to thank Messrs. T. Kono, M. Hayashi and M. Hayakawa for their assistance in the experimental work.

Zusammenfassung—Mikrogrammengen Eisen, Kobalt, Kupfer, Zink und Cadmium werden mit verschiedenen wäßrigen, organischen und gemischten Lösungsmitteln aus den Chloriden von Natrium, Kalium, Nickel, Cadmium, Barium und Blei extrahiert, die durch Eindampfen wäßriger Probenlösungen gewonnen wurden. Ein Ultraschallfeld beschleunigt die Extraktion. In mehreren Systemen erreicht man in annehmbarer Zeit zufriedenstellende Trennfaktoren und Ausbeuten an Spurenelement. Anwendungen auf eine polarographische Bestimmung und ein zweistufiges Abtrennverfahren werden beschrieben.

Résumé—On extrait des quantités de l'ordre du microgramme de fer, cobalt, cuivre, zinc et cadmium avec divers solvants aqueux, organiques et mixtes à partir des chlorures de sodium, potassium, nickel, cadmium, baryum et plomb préparés par évaporation de solutions aqueuses d'échantillons. Un champ ultra-sonore accélère l'extraction, et l'on obtient des récupérations de traces et des facteurs de séparation satisfaisants pour plusieurs systèmes dans un temps raisonnable. On décrit aussi l'application à un dosage polarographique et une technique de séparation à deux stades.

REFERENCES

1. A. Mizuike, in G. H. Morrison, ed., *Trace Analysis: Physical Methods*, p. 103. Wiley-Interscience, New York, 1965.
2. J. Minczewski, in W. W. Meinke and B. F. Scribner, eds., *Trace Characterization: Chemical and Physical* (*Natl. Bur. Stds. Monograph* 100), p. 385. National Bureau of Standards, Washington, D.C., 1967.
3. J. Rynasiewicz, M. P. Sleeper and J. W. Ryan, *Anal. Chem.*, 1954, **26**, 935.
4. G. H. Morrison and R. L. Rupp, *ibid.*, 1957, **29**, 892.
5. D. C. Newton, J. Sanders and A. C. Tyrrell, *Analyst*, 1960, **85**, 870.
6. A. Mizuike and T. Kono, *Mikrochim. Acta*, 1970, 665.
7. A. Mizuike, H. Kawaguchi and T. Kono, *ibid.*, 1970, 1095.
8. A. Mizuike and K. Fukuda, *ibid.*, in the press.

ɪalanta, 1972, Vol. 19, pp. 539 to 547. Pergamon Press. Printed in Northern Ireland

SELECTIVE GAS-CHROMATOGRAPHIC DETECTION USING AN ION-SELECTIVE ELECTRODE—II*

SELECTIVE DETECTION OF FLUORINE COMPOUNDS

TSUGIO KOJIMA, MITSUNOJO ICHISE and YOSHIMITSU SEO
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

(*Received* 7 *June* 1971. *Accepted* 17 *September* 1971)

Summary—Components in samples are separated on a gas chromatography column using hydrogen as carrier gas. The individual components from the column are passed through a platinum tube heated at 1000°, where they undergo hydrogenolysis, and fluorine compounds are converted into hydrogen fluoride. The hydrogen fluoride is dissolved in a slow stream of an absorption solution, and the fluoride ion concentration in the resulting solution is monitored in a flow-cell with a fluoride ion electrode. The potentiometric output of the cell is converted into a signal, which is proportional to the concentration of fluoride ion, by an antilogarithmic converter, and recorded. The response of the detector to fluorine compounds was about 10,000 times that to an equal quantity of other organic compounds, and 5×10^{-11} mole of fluorobenzene could be detected.

SEPARATE components from a gas chromatographic column are generally identified by determining the retention value. In practice, however, identification by the retention value alone is difficult and the final confirmation is often possible only after information on the elemental composition, functional groups and structure is obtained by simultaneously using other analytical means. One method used for this purpose is to transfer the eluates of pure components from the chromatograph into a spectrometer (infrared, mass or nuclear magnetic resonance), which thus produces the spectrum of each pure component in turn. The most effective is the combination of gas chromatograph and mass spectrometer.

Another method, which dispenses with expensive instruments uses the retention value and additional information obtained from the gas chromatogram above. Volatile injected compounds are reacted with non-volatile reagents to form non-volatile products in the gas chromatographic system and a comparison of chromatograms run in the presence and absence of the reagent is used to identify the kind of functional group or the structure of the carbon skeleton. Another method of this type is based on the selective detection of the compound containing a specific element or having a specific functional group, by means of a selective detector.

We have searched[1-3] for a method of this type which will give information on the elemental composition as well as the retention value. This is achieved by the selective detection of compounds containing halogens, sulphur, nitrogen and oxygen, with a reaction column and a selective detector. A new detection system for a gas chromatograph was recently devised, using an ion-selective electrode as a detecting element.[4] This system will not only detect organic compounds selectively but also furnish information on the composition.

---

* Part I: *Bunseki Kagaku*, 1971, 20, 20.

It is difficult to detect fluorine compounds selectively, and the only method[5] known so far is to monitor the intensity of the atomic emission spectrum of fluorine, using a d.c. discharge detector. The present method uses a simpler apparatus.

EXPERIMENTAL

Principle of the method

The sample components are separated on a gas chromatographic column using hydrogen as carrier gas and the effluent is passed through a platinum tube at 1000° where the separated components undergo hydrogenolysis and the fluorine in the fluorine compound is converted into hydrogen fluoride. The decomposition gases are introduced into an absorption tube where solution (flowing at a constant rate) absorbs the hydrogen fluoride. The solution emerging from the absorption tube is passed into a micro-cell equipped with a fluoride ion electrode. Changes in the fluoride ion concentration in the solution are detected by the corresponding changes in the ion electrode potential.[6] When the ionic strength is kept constant, a Nernst relationship exists between the electrode potential and the logarithm of the ion concentration. The difference in potential between the ion electrode and a reference electrode is fed to an antilog converter circuit and a signal directly proportional to the ion concentration is recorded. A chromatogram composed of only the peaks due to fluorine compounds is obtained.

Apparatus and procedure

A schematic diagram is shown in Fig. 1: (*a*) is the carrier gas source (hydrogen at a flow-rate of 25–48 ml/min), (*b*) and (*c*) represent a Yanagimoto Model GCG-II gas chromatograph, and (*d*) is an electric furnace, 200 mm in length, for elemental analysis which was operated at 1000°. A platinum tube, 2 m long and 1·5 mm inside diameter, was used as a pyrolysis tube (*e*); (*f*) is a glass absorption tube consisting of a gas-liquid contact area, 1 mm inside diameter and 0·15 m high, and a gas-liquid separation area, 13 mm inside diameter and 25 mm high. The pyrolysis tube and absorption tube are connected with 1 mm bore polyethylene tubing. Absorption solution (*g*) is pumped by a micro-pump (*h*) at a constant flow-rate (0·6 ml/min) *via* a stream buffer (*i*) to the absorption tube where it absorbs hydrogen fluoride *etc* from the hydrogenolysis gases. The unabsorbed gases such as methane are separated, together with the carrier gas, from the absorption solution in the gas-liquid separator and vented from the system. The emerging absorption solution is led through a measuring cell equipped with a fluoride ion electrode (*j*) as a detecting element and is then discarded. The absorption solution and the reference electrode (*k*) (a sleeve-type saturated calomel electrode) are connected by means of a saturated potassium chloride solution–agar bridge. The measuring cell is shown in detail in Fig. 2. Since the volume of the cell is about 0·05 ml, the dead time is about 5·0 sec when the flow rate of the absorption solution is 0·6 ml/min.

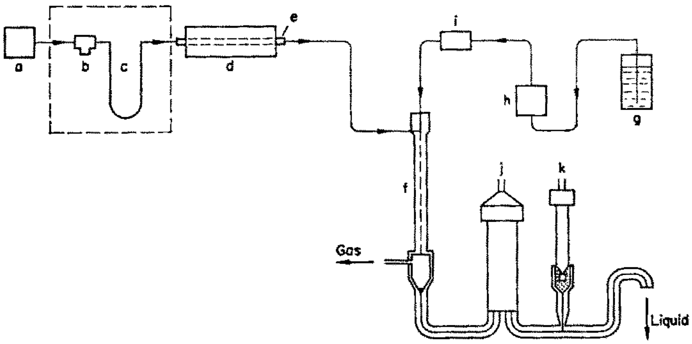


FIG. 1.—Schematic diagram of the apparatus.

The fluoride ion electrode used was an Orion Model 94-09A constructed from a single crystal membrane of lanthanum fluoride and it shows a potential *E* for a fluoride ion activity a_{F^-} in the vicinity of the electrode, in accordance with the Nernst equation as follows:

$$F = E_0 - 2{\cdot}303 \frac{RT}{\mathrm{F}} \log a_{F^-} \qquad (1)$$

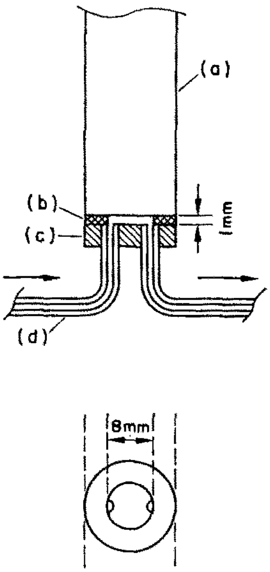


FIG. 2.—Cell details.
(*a*) Fluoride ion electrode body; (*b*) silicone rubber packing; (*c*) polyethylene plate; (*d*) glass capillary

If the ionic strength of the absorption solution is kept constant, a negative potential proportional to the logarithm of the fluoride ion concentration C_{F^-} is obtained:

$$E = E_0' - 0{\cdot}0592 \log C_{F^-} \quad \text{(at 25°)} \tag{2}$$

The circuit for measuring the electrode potential is shown in Fig. 3, where (*a*) is a voltage follower using a QFT-2a amplifier (Philbrick/Nexus Research) as an impedance converter, (*b*) is an adjustable-coefficient inverter (Philbrick PF-85AU inversion type negative feedback coupling) as an adapter for (*c*), an antilog converter, (Philbrick/Nexus Model 4351); (*d*) is a 1-mV recorder (Shimadzu R201) and (*e*) is the signal input.

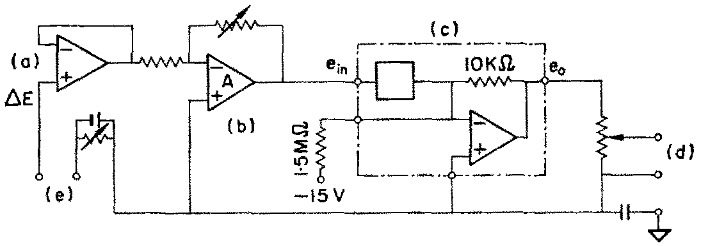


FIG. 3.—Circuit for ion electrode detector.

In order to use the fluoride ion electrode in the Nernstian range, a small amount of sodium fluoride was added to the absorption solution to make the concentration of fluoride ion approximately $10^{-5}M$. If this concentration of fluoride ion is C_b, the electrode potential is

$$E = E_0' - 0{\cdot}0592 \log C_b \tag{3}$$

The potential E' when hydrogen fluoride is absorbed in this solution and the concentration of fluoride ion is increased by ΔC is given by

$$E' = E_0' - 0{\cdot}0592 \log (C_b + \Delta C) \tag{4}$$

From equations (3) and (4), the change in the potential, ΔE, corresponding to the change in the fluoride ion concentration is given by

$$\Delta E = (E' - E) = -0\cdot0592 \log \left(1 + \frac{\Delta C}{C_b}\right) \tag{5}$$

In this apparatus, the potential change is recorded after antilog conversion to give an output signal proportional to the concentration, as in the case of an ordinary detector, the antilog converter used having the following conversion characteristics:

$$e_0 = -\frac{1}{10} \,.\, 10^{0\cdot5}e_{in} \tag{6}$$

The change in potential, ΔE, enters as input e_{in} to the antilog converter (*c*) after undergoing impedance conversion in the voltage follower (*a*) and is then amplified A times in the amplifier (*b*). Therefore,

$$e_{in} = -A \,.\, \Delta E \tag{7}$$

The following equation is derived from equations (5), (6) and (7):

$$\begin{aligned} e_0 &= -\frac{1}{10} \,.\, 10^{-0\cdot5} \,.\, A \,.\, \Delta E \\ \log(-e_0) &= -1 + 0\cdot5 \,.\, A \,.\, 0\cdot0592 \log \left(1 + \frac{\Delta C}{C_b}\right) \end{aligned} \tag{8}$$

Adjustment of the gain A in the amplifier (*b*) in such a manner as to make the coefficient of the second term of the right-hand side of equation (8) unity, that is to make $A = 33\cdot78$, gives the relationship

$$e_0 = -\frac{1}{10}\left(1 + \frac{\Delta C}{C_b}\right) \tag{9}$$

and the output e_0 of the antilog converter begins to change in direct proportion to the change in the fluoride ion concentration in the absorption solution.

RESULTS AND DISCUSSION

Samples containing hydrocarbons, nitrogen and oxygen compounds in addition to fluorine compounds were prepared and the possibility of selective detection of fluorine compounds was investigated.

Aliphatic compounds

In Fig. 4 is shown a chromatogram obtained by injecting into the column 0·1–0.2 μl of sample consisting of a mixture of 0·01 mole each of ethylmercaptan, n-octane, 1,2-dibromoethane and 1-nitropropane and 0·1 mmole of ethyl trifluoroacetate. In Fig. 4, (*a*) is an ordinary non-selective chromatogram obtained by passing the effluent component from the separation column through a hydrogen flame ionization detector while by-passing the hydrogenolysis tube, and the number in parentheses indicates the mole ratio; (*b*) is a chromatogram obtained by subjecting the same sample to hydrogenolysis absorbing the decomposition gas in the TISAB solution[7] (a mixture of 57 ml of glacial acetic acid, 58 g of sodium chloride and 0·3 g of sodium citrate, diluted to 2 l.) which is about $10^{-5}M$ in sodium fluoride as mentioned above. The ethyl trifluoroacetate is selectively detected in the measuring cell.

In measurements of fluoride ion concentration with the aid of the fluoride ion electrode, it should be noted that the interfering OH^- ions will show their effect as the pH of the solution rises whereas the apparent F^- concentration will decrease owing to formation of HF or HF_2^- as the pH drops. The useful range of pH is 5–7

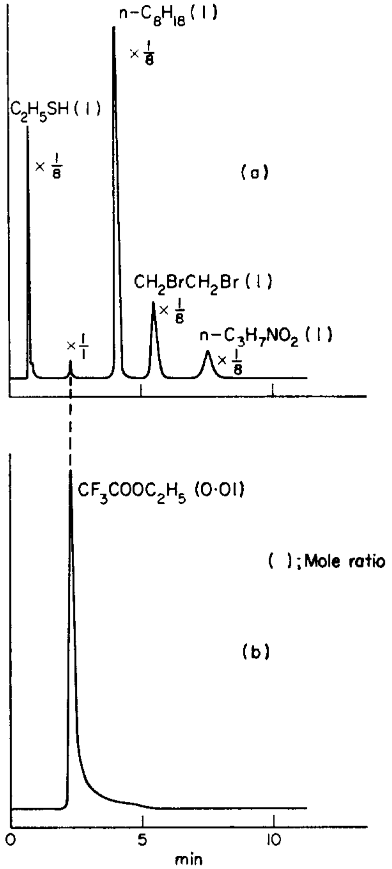


FIG. 4.—Chromatogram of a test mixture.
Column—Durapak-Carbowax 400/Porasil C (100–120 mesh), 1 m; temperature—90°; carrier gas—H_2 28 ml/min. (*a*) Non-selective detection by use of FID; (*b*) selective detection of fluorine compound by use of fluoride ion electrode detector.

when the concentration of F^- is $10^{-5}M$, according to Bock,[8] and a TISAB solution of pH 5 is used as an absorption solution.

By use of the same procedure, 0·1 mmole in 1,1,2,2-tetrachloro-1,2-difluoroethane was detected selectively in a mixture with 0·01 mole each of ethyl iodide, n-propyl acetate, 1,1,2-trichloroethane and ethyl thiocyanate.

Aromatic compounds

A chromatogram of a mixture of 0·01 mole each of ethylbenzene, bromobenzene, benzonitrile and thioanisole and 0·1 mmole of *o*-fluorotoluene is shown in Fig. 5. For further confirmation, a mixture of 0·01 mole each of *o*-xylene, *o*-chlorotoluene, methyl benzoate, phenyl isothiocyanate and 0·1 mmole of benzotrifluoride was chromatographed. It was confirmed from these experiments that selective detection of fluorine compounds is complete.

Quantitative results

The results shown in Fig. 4 and Fig. 5 indicated that fluorine compounds could be detected selectively, and the quantitativeness of response of the detector was next investigated. The results are shown in Table I.

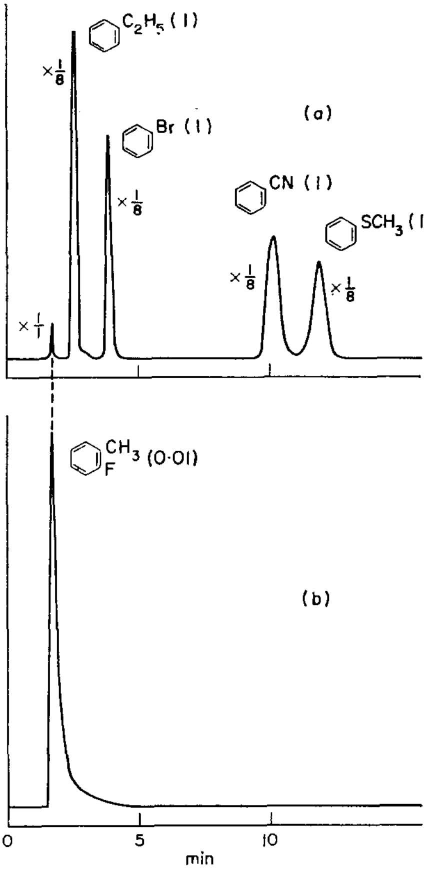
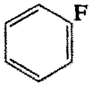
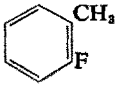
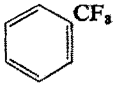
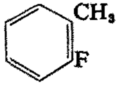
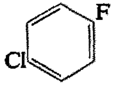
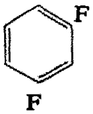


FIG. 5.—Chromatogram of a test mixture.
Column temperature 128°; see Fig. 4 for other conditions. (*a*) Non-selective detection by use of FID, (*b*) selective detection of fluorine compound by use of fluoride ion electrode detector.

Fluorobenzene, *o*-fluorotoluene, and benzotrifluoride were chosen as the first group of compounds; a sample containing 0·01 mole each of these compounds was prepared, diluted 10,000-fold with n-hexane, and 2 μl were injected into a column (Durapak-Carbowax 400/Porasil C, 100–120 mesh, 1 m, 60°), and chromatographed. The relative size of each peak area was determined by the method of cutting out the recorded peaks and weighing the paper. Taking benzotrifluoride as the standard, the ratio of the peak area of each of two other components to the peak area of the standard was measured repeatedly. 1,1,2,2-Tetrachloro-1,1-difluoroethane, *o*-fluorotoluene, and *p*-chlorofluorobenzene were chosen as the second group of compounds; a sample containing 0·01 mole each of these compounds and diluted 10,000-fold with n-hexane, was chromatographed as before. The same procedure as for the first

TABLE I.—COMPARISON OF RESPONSES OBTAINED FROM SEVERAL FLUORINE COMPOUNDS

	First group			Second group			Third group		
Sample				CCl_2FCCl_2F			$C_6F_{11}CF_3$	C_6F_6	
Mole ratio	1	1	1	1	1	1	$\frac{1}{7}$	$\frac{1}{3}$	1
Number of fluorine atoms	1	1	3	2	1	1	14	6	2
Ratio of peak areas	0·33 0·36 0·32 0·31 0·32 0·31 0·31 0·31 0·33 0·32	0·32 0·32 0·32 0·34 0·31 0·32 0·33 0·33 0·32 0·32	1 1 1 1 1 1 1 1 1 1	1 1 1 1 1 1 1 1 1 1	0·49 0·48 0·41 0·47 0·51 0·50 0·45 0·44 0·49 0·46	0·49 0·49 0·44 0·48 0·50 0·51 0·45 0·47 0·48 0·47	1·02 0·98 0·99 0·93 0·99 0·99 0·97 1·04 0·98 0·96	1 1 1 1 1 1 1 1 1 1	1·02 1·03 0·97 0·96 1·04 1·04 1·03 1·05 0·97 0·97
Average	0·322	0·323	1	1	0·470	0·478	0·985	1	1·008

group was repeated with 1,1,2,2-tetrachloro-1,2-difluoroethane as the standard. Perfluoro-compounds were chosen as the third group of compounds; a sample containing 1/350 mole of perfluoromethylcyclohexane, 1/150 mole of perfluorobenzene and 1/50 mole of *m*-difluorobenzene was prepared and diluted 1000-fold with n-hexane, and 0·8 μl was chromatographed. The perfluorobenzene was used as the standard.

If the hydrogenolysis reaction, the absorption of hydrogen fluoride, and the response of the detector to fluoride ions are quantitative, the ratio of the peak areas of the three components for each group should be proportional to the number of fluorine atoms in each molecule. The average of the experimentally determined ratio of peak areas is close to the theoretical value. It is thus shown that fluorine bonded to an aromatic nucleus (which has been said to be particularly resistant to quantitative decomposition), perfluoro-compounds of the third group, and compounds containing other halogens in addition to fluorine can be determined quantitatively.

As mentioned previously, a proportionality to the fluoride ion concentration in the absorption solution should exist in the present apparatus in the range where the ionic strength of the absorption solution is constant. To confirm this, experiments were carried out with fluorobenzene as a sample.

The output e_0 of the antilog converter is confined to the range from 0 to -10 V. Therefore, supposing the concentration of the fluoride ion added to the absorption solution is $10^{-5}M$, the permissible range of the fluoride ion concentration in the absorption solution becomes 10^{-5}–$10^{-3}M$ from equation (9). The ionic strength μ of the absorption solution is 0·820, and this changes merely to 0·821 when the fluoride ion concentration reaches $10^{-3}M$ upon absorption of hydrogen fluoride. As a consequence, the changes in the activity coefficient of the fluoride ion may be ignored. Moreover, the changes in the pH are negligible. Therefore, if the amount of sample is adjusted so that the fluoride ion concentration falls within the range 10^{-5}–$10^{-3}M$, there should exist a linear relationship between the amount of sample injected and the peak area. Accordingly, solutions of fluorobenzene in n-hexane with a concentration of 0·0001–0·05M were prepared, 2 μl of each were injected into the column, and the relationship between the amount of sample injected and the peak area was examined. An absolute calibration curve was obtained and the existence of a linear relationship between the amount of sample injected (2×10^{-10}–10^{-7} mole) and the peak area in the concentration range indicated above was found.

CONCLUSION

A gas chromatographic detector with using an ion-selective electrode has been developed and applied to the selective detection of fluorine compounds. It has the following advantages: the limit of detection is 5×10^{-11} mole (for fluorobenzene), the detector sensitivity is high, the degree of selectivity is 10,000 or more with an extremely high sensitivity, the drift of the base line is 0·02 mV/hr with good stability.

The response time of the detector is about 10 sec when the concentration of F^- is about $10^{-5}M$ and several seconds when it is more than $10^{-4}M$. Such slow responses distort the early peaks slightly but the effect is negligible for peaks having retention times greater than 5 min.

A platinum tube was used as a hydrogenolysis tube in the present study, but could be replaced by a quartz tube.

Zusammenfassung—Die Proben werden an einer Gaschromatographiesäule mit Wasserstoff als Trägergas in ihre Komponenten getrennt. Die einzelnen von der Säule kommenden Komponenten werden durch ein auf 1000° geheiztes Platinrohr geleitet; dort werden sie hydrierend gespalten. Fluorverbindungen werden in Fluorwasserstoff übergeführt. Der Fluorwasserstoff wird in einem langsamen Strom einer Absorptionslösung gelöst und die Fluoridkonzentration in der Lösung in einer Durchflußzelle mit einer Fluoridionen-Elektrode verfolgt. Das potentiometrische Verhalten der Zelle wird mit Hilfe eines antilogarithmischen Umsetzers in ein Signal umgesetzt, das der Fluoridkonzentration proportional ist, und registriert. Der Detektor sprach auf Fluorverbindungen etwa 10 000-mal stärker an als auf eine gleiche Menge anderer organischer Verbindungen; $5 \cdot 10^{-11}$ Mol Fluorbenzol konnten nachgewiesen werden.

Résumé—On sépare des composants dans des échantillons sur une colonne de chromatographie en phase gazeuse en utilisant l'hydrogène comme gaz vecteur. On fait passer les composants individuels provenant de la colonne à travers un tube de platine chauffé à 1000°, où ils subissent l'hydrogénolyse, et les composés fluorés sont convertis en acide fluorhydrique. L'acide fluorhydrique est dissous dans un lent courant d'une solution d'absorption, et la concentration en ion fluorure dans la solution résultante est contrôlée dans une cellule à écoulement avec une électrode à ion fluorure. L'émission potentiométrique de la cellule est convertie en un signal, qui est proportionnel à la concentration en ion fluorure, par un convertisseur antilogarithmique, et enregistré. La réponse du détecteur aux composés fluorés est d'environ 10 000 fois celle fournie par une égale quantité d'autres composés organiques, et l'on a pu détecter 5×10^{-11} mole de fluorobenzène.

REFERENCES

1. W. Funasaka, T. Kojima and Y. Seo, *Bunseki Kagaku*, 1968, **17**, 464.
2. T. Kojima, Y. Seo and J. Nishida, *ibid.*, 1968, **17**, 1496.
3. T. Kojima, M. Ichise and Y. Seo, *ibid.*, 1969, **18**, 1460.
4. *Idem*, *ibid.*, 1971, **20**, 20.
5. R. S. Braman and A. Dynako, *Anal. Chem.*, 1968, **40**, 95.
6. E. Pungor, *ibid.*, 1967, **39** (13), 28A.
7. M. S. Frant and J. W. Ross, *ibid.*, 1968, **40**, 1169.
8. R. Bock and S. Strecker, *Z. Anal. Chem.*, 1968, **235**, 322.

Talanta, 1972, Vol. 19, pp. 549 to 557. Pergamon Press. Printed in Northern Ireland

POLAROGRAPHIC STUDIES OF CADMIUM, ZINC AND MANGANESE(II) IODIDE COMPLEXES IN ACETONITRILE

S. Misumi and M. Aihara
Inorganic Chemistry Laboratory, Faculty of Science
Kyushu University, Fukuoka, Japan

(*Received* 15 *June* 1971. *Accepted September* 1971)

Summary—Cadmium, zinc and manganese(II) iodide complexes have been studied polarographically in acetonitrile and the electrode reactions for these complexes discussed. The overall stability constants of the iodide complexes of these metal ions were evaluated and corrected for the effect of the ion-pairing electrolyte. The values for log β_4 of CdI_4^{2-} and ZnI_4^{2-} are 26·2 and 18·4 respectively and the values found for the Mn(II) iodide complex are log $\beta_1 = 3·5$, log $\beta_2 = 5·6$, log $\beta_3 = 7·8$, log $\beta_4 = 10·0$, log $\beta_5 = 12·2$ and log $\beta_6 = 14·4$. Within certain limits, the wave-height for each complex is proportional to the metal concentration.

THE POLAROGRAPHIC behaviour of some halide complexes in dimethylsulphoxide and dimethylformamide has been studied by Pool[1] and by Furlani *et al.*[2] respectively, but there are very few investigations on the stability constants of halide complexes in these non-aqueous solvents, because of the problems associated with the unknown activities. This work deals with the electrode reactions for iodide complexes of cadmium, zinc and manganese(II) and the stability constants of iodide complexes of these metal ions in acetonitrile (which has the low donor number[3] of 14·1).

EXPERIMENTAL

Materials

Acetonitrile (AN) (Wako Junyaku Co., extra pure reagent grade) was purified[4] and the water content was found by Karl Fischer titration to be 0·01%. There was no impurity causing a detectable polarographic current at potentials less than −2·8 V *vs.* SCE.

Reagent-grade cadmium, zinc and manganese(II) perchlorate hexahydrates were dried *in vacuo* at 60° for 5–6 days.

Tetraethylammonium iodide, Et_4NI, was prepared, purified three times and dried *in vacuo* at 60° for 5–6 days. Et_4NClO_4 (TEAP) was used as the supporting electrolyte.

Apparatus

The electrolysis cell consists of three electrodes as shown in Fig. 1. The dropping mercury electrode had the following characteristics: $m = 1·425$ mg/sec, $t = 3·79$ sec in 0·1*M* TEAP–AN medium at −0·5 V *vs.* SCE. A platinum wire was used as the counter-electrode. The reference electrode was SCE with a salt bridge ($NaClO_4$–NaCl–KCl agar bridge). The temperature was controlled at 25·0 ± 0·1°. The junction potential was about 10 mV.

Procedure

A sample solution in TEAP–AN, 0·5m*M* in metal(II) perchlorate and containing an appropriate amount of Et_4NI, was taken in a cell. Since there is appreciable ion-pairing of the tetraethylammonium ion with iodide, the concentration of Et_4N^+ was kept constant (0·1*M*) for each metal iodide solution by adding an appropriate amount of Et_4NClO_4 instead of using constant ionic strength. The concentration of free iodide was calculated by using the ion-dissociation constant[5,6]

$$(K_d)_{Et_4NI} = 0·2.$$

Et_4NClO_4 was assumed to be almost completely dissociated.[7,8]

The dissolved oxygen in the solution was removed by bubbling for 20 min with pure nitrogen presaturated with acetonitrile vapour; the polarogram was then recorded.

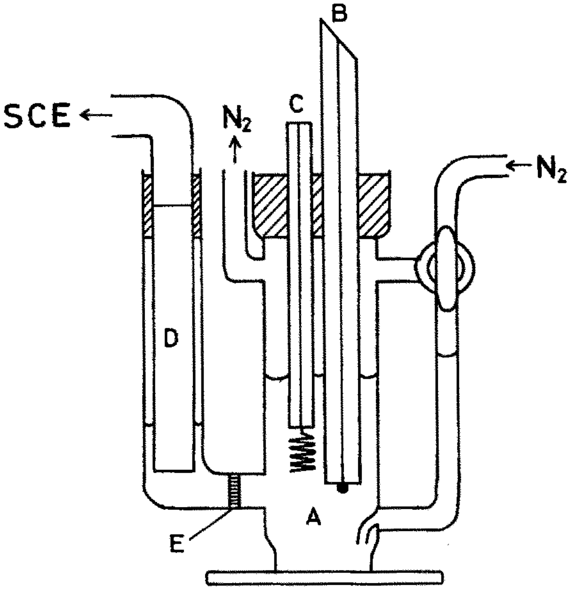


FIG. 1.—Electrolysis cell.
A, sample solution *B*, DME
C, counter-electrode *D*, salt-bridge
E, sintered glass

THEORY

DeFord and Hume[9] derived the equation for the shift of the half-wave potential at constant ionic strength and defined the function $F_p(X)$, assuming that the complex species, $(MX_p^{(n-p)+} \ldots)$ dissociate to M^{n+} rapidly and are reduced reversibly to amalgam, that is

$$F_0(X) = \sum_0^p \beta_p[X]_0^p = \text{antilog}\left\{\frac{n}{0{\cdot}0591}\left[(E_{1/2})_s - (E_{1/2})_c\right] + \log\frac{k_s}{k_c}\right\} \tag{1}$$

where $(E_{1/2})_s$ and $(E_{1/2})_c$, k_s and k_c are the half-wave potentials and diffusion-current constants of the simple ion and complex ion, respectively, n denotes the number of electrons involved in the reduction, β_p is the overall formation constant of the pth complex and $[X]_0$ is the concentration of the complexing ligand at the electrode surface; concentrations are used instead of activities. The $F_p(X)$ functions can be written in the following forms if the ionic strength is kept constant.

$$F_1(X) = \frac{F_0(X) - \beta_0}{[X]_0}\ (\beta_0 = 1),$$

$$F_2(X) = \frac{F_1(X) - \beta_1}{[X]_0}$$

$$F_p(X) = \frac{F_{p-1}(X) - \beta_p}{[X]_0} \tag{2}$$

According to Bjerrum[10] the average number $\bar{p}$ of ligands attached is then given by equation (3).

$$\bar{p} = \frac{\mathrm{d}\ln F_0(\mathrm{X})}{\mathrm{d}\ln [\mathrm{X}]_0} = -\frac{\mathrm{d}(E_{1/2})_c}{\mathrm{d}\log [\mathrm{X}]_0}\Big/\frac{0{\cdot}0591}{n} \tag{3}$$

Values of $F_p(\mathrm{X})$ for various concentrations $[\mathrm{X}]_0$ of the complexing ligand can be determined experimentally and equations (1) and (2) solved graphically for β_1, $\beta_2, \ldots, \beta_p$.

If $\mathrm{MX}_p^{(n-p)+}$ is predominant in the solution because of a large value of β_p, equation (1) can be simplified to the equation derived by Lingane.[11]

$$\beta_p[\mathrm{X}]_0^p = \operatorname{antilog}\left\{\frac{n}{0{\cdot}0591}\,[(E_{1/2})_s - (E_{1/2})_c] + \log\frac{k_s}{k_c}\right\} \tag{4}$$

The values of p and β_p are then obtained from plots of $\Delta E_{1/2}$[i.e. $(E_{1/2})_s - (E_{1/2})_c$] *vs.* log $[\mathrm{X}]_0$.

In a solvent of low dielectric constant, the concentration of ligand must be corrected for ion-pair formation by the ligand. The total concentration C_x of the complexing ligand is given by

$$C_x = [\mathrm{X}]_0 + [\mathrm{M}]_0 \sum_1^p p\beta_p[\mathrm{X}]_0^p + [\text{ion-pair}]_0 \tag{5}$$

where $[\text{ion-pair}]_0$ is the concentration of the complexing ligand ion-pairs at the electrode surface. When $E = E_{1/2}$, equation (5) becomes

$$C_x = [\mathrm{X}]_0 + \frac{[\mathrm{M}]_t}{2F_0} \sum_1^p p\beta_p[\mathrm{X}]_0^p + [\text{ion-pair}]_0 \tag{6}$$

where subscript t means total concentration. The dissociation constant k_d of $\mathrm{Et_4NX}$ is given by $k_d = [\mathrm{Et_4N^+}]_t[\mathrm{X}]_0/[\mathrm{Et_4NX}]_t$. For a given series of experiments at constant $[\mathrm{Et_4N^+}]$, the ion-pair concentration is given by

$$[\text{ion-pair}]_0 = [\mathrm{Et_4NX}]_t = [\mathrm{Et_4N^+}]_t[\mathrm{X}]_0/k_d. \tag{7}$$

From equations (6) and (7):

$$[\mathrm{X}]_0 = \left\{C_x - \frac{[\mathrm{M}]_t}{2F_0}\sum_1^p p\beta_p[\mathrm{X}]_0^p\right\}\Big/\left(1 + \frac{[\mathrm{Et_4N^+}]_t}{k_d}\right). \tag{8}$$

A simultaneous solution to equations (1) and (8) cannot easily be obtained. However, when $\mathrm{MX}_p^{(n-p)+}$ is predominant in solution, equation (8) simplifies to

$$[\mathrm{X}]_0 = \left\{C_x - \frac{p}{2}\,[\mathrm{M}]_t\right\}\Big/\left(1 + \frac{[\mathrm{Et_4N^+}]_t}{k_d}\right). \tag{9}$$

Assuming the free halide ion concentration to be

$$[\mathrm{X}]_0 \sim [\mathrm{X}]_t = C_x/\{1 + [\mathrm{Et_4N^+}]_t/k_d\},$$

the value of p is obtained graphically [equation (3)] and the approximate $[\mathrm{X}]_0$ is calculated by using equation (9). This procedure is repeated and finally with the refined $[\mathrm{X}]_0$ the true values of the β's are obtained graphically from the $F_p(\mathrm{X})$ plots.

The method can be applied to reversible electrode reactions of simple and complex ions. For the quasi-reversible electrode process, the reversible half-wave potential, $(E_{1/2})^r$ can be calculated by applying the Matsuda–Ayabe theory.[12]

RESULTS AND DISCUSSION

For each metal iodide complex system the electrode reaction was reversible or quasi-reversible, two-electron and diffusion-controlled. The ion-pair dissociation constant for $Et_4N^+I^-$ was used to correct the free iodide ion concentration. The overall stability constants obtained are concentration constants rather than activity constants.

Cd–I⁻ system

The reduction wave of 0·5m*M* cadmium was split into two waves by addition of iodide (Fig. 2). The height of the first wave (simple ion) and that of the second wave (complex ion) were almost the same at $[I^-]_t/[Cd]_t = 1$. The first wave disappeared at $[I^-]_t/[Cd]_t = 4$, but the second wave was left (reciprocal slope: 0·044 V). The reciprocal slope for the complex wave was about 0·030 V at $[I^-]_t/[Cd]_t \gg 10$ and the electrode reaction was reversible. As shown in Table I, the half-wave potential was shifted to more negative values with increasing concentration of iodide ion and the height of this wave decreased slightly.

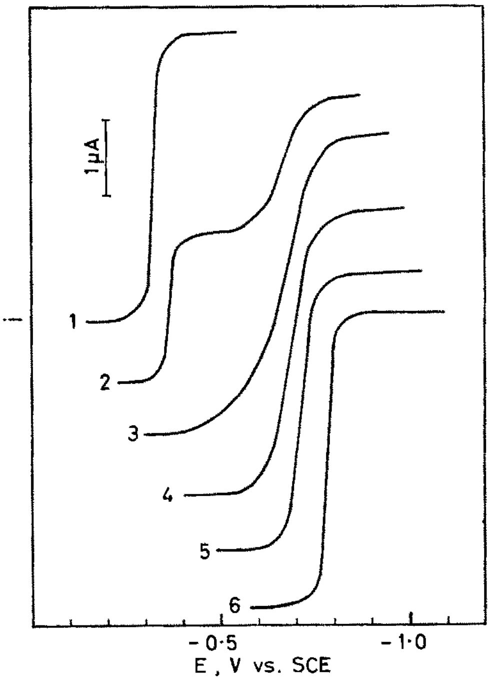


FIG. 2.—Polarograms of 0·50m*M* Cd in the presence of iodide. $[I^-]_t/[Cd]_t$: *1*—0; *2*—1; *3*—2; *4*—3; *5*—4; *6*—10.

The plot of log $[I^-]$ *vs.* $\Delta E_{1/2}$ is shown in Fig. 3. The dashed line shows a plot of the values obtained by using $[I^-]_t = C_{Et_4NI}/(1 + [Et_4N^+]_t/k_d)$ and this plot was found to be linear at $[I^-]_t > 4$m*M*. The value of *p* was calculated to be about 4·3.

TABLE I.—POLAROGRAPHIC DATA FOR Cd–I^- SYSTEM

$[I^-]_t$, *mM*	$-E_{1/2}$, *V vs.* SCE	*i*, *μA*	Reciprocal slope, *mV*
0	0·275	3·88	28
0·5	0·291	1·91	29
	0·630	1·74	—*
1·0	—†		
1·5	0·675	3·84	56
2·0	0·701	3·77	44
3·0	0·735	3·69	33
4·0	0·758	3·72	31
5·0	0·768	3·80	30
10·0	0·811	3·18	28
15·0	0·836	3·58	28
20·0	0·847	3·23	27
30·0	0·869	3·06	29
40·0	0·881	2·77	29

$[Cd]_t = 0{\cdot}5mM$
* Plot not made.
† Ill-defined.

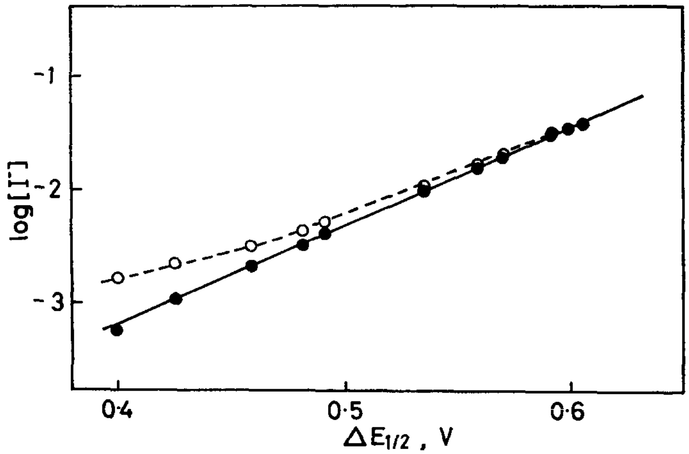


FIG. 3.—Plot of log $[I^-]$ *vs.* $\Delta E_{1/2}$ for Cd–I^- system.
--○-- log $[I^-]_t$ *vs.* $\Delta E_{1/2}$
—●— log $[I^-]_0$ *vs.* $\Delta E_{1/2}$

Then $[I^-]_0$ was calculated again by using equation (9) with $p = 4$. The full line shows the plot of these values to be linear. The value of p was calculated to be $3{\cdot}9_7$. As $0{\cdot}059/2 \log k_s/k_c < 0{\cdot}005$ V under these conditions, this term can be neglected within experimental error.

Extrapolation of the plot of log $[I]_0$ *vs.* $\Delta E_{1/2}$ to $1M$ concentration of $[I]_0$ gave the value of $\Delta E_{1/2}$ for use in equation (4), and thence $\log \beta_4 = 26{\cdot}2$.

In AN, the values of successive formation constants for the cadmium–iodide complexes could not be obtained, because of the large formation constant of CdI_4^{2-}. The value of β_4 was found to be much larger in AN than that $(7{\cdot}17)^{13}$ in formamide.

Zn–I⁻ system

This system behaved similarly to the cadmium system, and gave the value $\log \beta_4 = 18{\cdot}4$ for ZnI_4^{2-}.

There are few data for zinc–iodide complexes, and this complex seems, in general, to be unstable in aqueous solution. The polarographic data are given in Table II.

TABLE II.—POLAROGRAPHIC DATA FOR Zn–I⁻ SYSTEM

$[I^-]_t$, *mM*	$-E_{1/2}$, *V vs.* SCE	*i*, *μA*	Reciprocal slope, *mV*
0	0·648	3·57	30
0·5	*		
1·0	0·823	3·63	58
1·5	0·855	3·62	41
2·0	0·866	3·47	37
5·0	0·923	3·20	32
10·0	0·944	2·96	28
15·0	0·965	2·85	27
20·0	0·978	2·48	29
25·0	0·987	2·05	27
30·0	0·994	2·05	28
35·0	0·998	1·94	29

$[Zn(II)]_t = 0{\cdot}5$m*M*

* Ill-defined.

Mn(II)–I⁻ system

Polarograms of 0·5m*M* manganese(II) in the presence of iodide ion did not exhibit the wave-splitting. The half-wave potential was constant (−1·14 V *vs.* SCE) at $[I^-]_t/[Mn(II)]_t \leqslant 4$ (Table III), but shifted to more negative potentials at $[I^-]_t/[Mn(II)]_t \geqslant 6$ and the height of the wave decreased slightly. A plot of *E vs.* $\log i/(i_d - i)$ indicates that the electrode reaction is quasi-reversible.

A plot of $[E + (2{\cdot}3RT/nF) \log i/(i_d - i)]$ *vs.* *E* is shown in Fig. 4. The reversible half-wave potential, $(E_{1/2})^r$, was obtained by extrapolation to a positive enough potential.

TABLE III.—POLAROGRAPHIC DATA FOR Mn(II)–I⁻ SYSTEM

$[I^-]_t$, *mM*	$-E_{1/2}$, *V vs.* SCE	$-E^r_{1/2}$, *V vs.* SCE	*i*, *μA*	Reciprocal slope, *mV*
0	1·148		3·17	30
1·0	1·149		3·33	28
2·0	1·146		3·21	30
3·0	1·159		3·33	35
5·0	1·177	1·171	3·37	*
10·0	1·239	1·222	3·15	*
15·0	1·259	1·241	3·25	*
20·0	1·292	1·269	3·15	*
25·0	1·312	1·290	3·06	*
30·0	1·336	1·310	2·97	*
35·0	1·356	1·317	2·97	*

$[Mn(II)]_t = 0{\cdot}5$m*M*

* Plot curved.

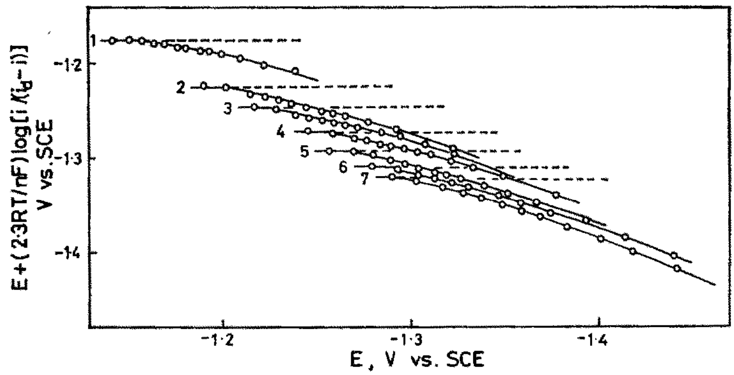


FIG. 4.—Plot of $\{E + 2{\cdot}3RT/nF \log i(i_d - i)\}$ *vs.* E for Mn(II) in the presence of iodide. $[\mathrm{I}^-]_t$: *1*—5·0; *2*—10·0; *3*—15·0; *4*—20·0; *5*—25·0; *6*—30·0; *7*—35·0m*M*.

The plot of $\Delta E_{1/2}[= (E_{1/2})_s - (E_{1/2})_c^{r}]$ *vs.* log $[\mathrm{I}^-]$ is shown in Fig. 5. The dashed line shows the plot of the values obtained by using $[\mathrm{I}^-]_t = C_{\mathrm{Et_4NI}}/(1 + [\mathrm{Et_4N^+}]/k_d)$. This plot is curved and indicates that some species of Mn(II)–iodide complex co-exist in acetonitrile. The value of $\bar{p}$ was calculated by using equation (3) at each point of the curve. Then the values of $[\mathrm{I}^-]_0$ were obtained by using equation (9), and $\Delta E_{1/2}$ *vs* log $[\mathrm{I}^-]_0$ was plotted. This procedure was repeated till the each value of $[\mathrm{I}^-]_0$ became constant. The full line in Fig. 5 shows the final plot. On substitution of these experimental data into the right-hand side of equation (1), the $F_0(\mathrm{X})$ function was calculated, and the $F_p(\mathrm{X})$ function was calculated from the previous $F_{p-1}(\mathrm{X})$ function by equation (2). Figure 6 shows the plot of F_p functions against iodide concentration, $[\mathrm{I}^-]_0$. By extrapolation of the $F_p(\mathrm{X})$ function to $[\mathrm{I}^-]_0 = 0$, the value of β_p was obtained.

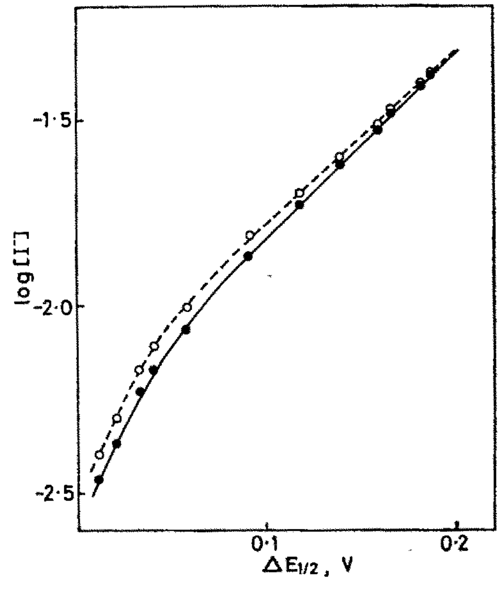


FIG 5.—Plot of log $[\mathrm{I}^-]$ *vs.* $\Delta E_{1/2}$ for Mn(II)-I⁻ system.
--○-- log $[\mathrm{I}^-]_t$ *vs.* $\Delta E_{1/2}$
—●— log $[\mathrm{I}^-]_0$ *vs.* $\Delta E_{1/2}$

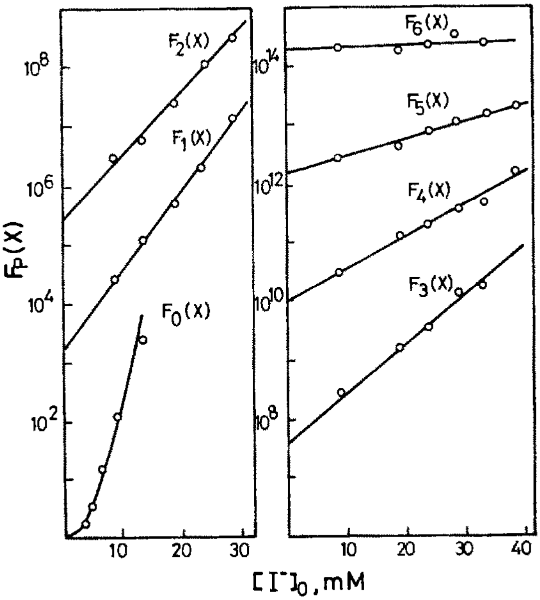


Fig. 6.—Plot of $F_p(X)$ *vs.* $[I^-]_0$ for Mn(II)–I^- system.

The logarithms of the overall formation constants for this system are:

$$\log \beta_1 = 3{\cdot}5, \quad \log \beta_2 = 5{\cdot}6, \quad \log \beta_3 = 7{\cdot}8$$
$$\log \beta_4 = 10{\cdot}0, \quad \log \beta_5 = 12{\cdot}2, \quad \log \beta_6 = 14{\cdot}4$$

In this procedure, extrapolation to zero concentration of complex is used so that the values of β_p can be obtained without using the value of the activity coefficient of the complexing ligand.

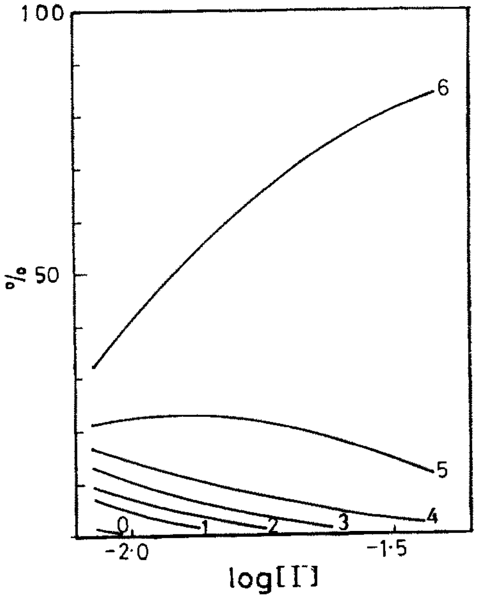


Fig. 7.—Distribution diagram for manganese iodide system. Number on the curve indicates number of ligands bound in complex

The value of p was calculated to be 6 in the range of high concentration of iodide ion as shown in Fig. 5. By use of equation (4), log β_6 was calculated at $[I^-]_0 =$ 38·5mM and found to be 14·8, in good agreement with the value obtained by the DeFord and Hume method. MnI_6^{4-} is the predominant species in acetonitrile medium.

The distribution of manganese(II)-iodide complexes in acetonitrile was calculated as a function of ligand concentration and is shown in Fig. 7.

In a mixture of cadmium, zinc and manganese(II) iodide complexes, each wave is clearly separated from the others and the wave-height for each complex is proportional to the metal concentration in the range from 0·1 to 1·0mM in acetonitrile medium.

Acknowledgements—The authors wish to express their sincere thanks to the Ministry of Education for its financial support of this work.

Zusammenfassung—Jodidkomplexe von Cadmium, Zink und Mangan(II) wurden polarographisch in Acetonitril untersucht und die Elektrodenreaktionen dieser Komplexe diskutiert. Die Bruttostabilitätskonstanten der Jodidkomplexe dieser Metallionen wurden ermittelt und für den Einfluß des ionenpaarbildenden Elektrolyten korrigiert. Die log β_4-Werte von CdI_4^{2-} und ZnI_4^{2-} betragen 26,2 bzw. 18,4; beim Mangan(II)-Jodidkomplex wurden log $\beta_1 = 3,5$, log $\beta_2 = 5,6$, log $\beta_3 = 7,8$, log $\beta_4 = 10,0$, log $\beta_5 = 12,2$ und log $\beta_6 = 14,4$ gefunden. In gewissen Grenzen ist die Stufenhöhe jedes Komplexes proportional zur Metallkonzentration.

Résumé—Les complexes d'iodure de cadmium, zinc et manganèse(II) ont été étudiés polarographiquement en acétonitrile et l'on discute des réactions à l'électrode de ces complexes. On a évalué les constantes de stabilité globales des complexes iodure de ces ions métalliques et les a corrigées pour l'influence d'appariement d'ions de l'électrolyte. Les valeurs de log β_4 de CdI_4^{2-} et ZnI_4^{2-} sont de 26,2 et 18,4 respectivement et les valeurs trouvées pour le complexe d'iodure de Mn(II) sont log $\beta_1 = 3,5$; log $\beta_2 = 5,6$; log $\beta_3 = 7,8$; log $\beta_4 = 10,0$; log $\beta_5 = 12,2$ et log $\beta_6 = 14,4$. Dans certaines limites, la hauteur de vague pour chaque complexe est proportionnelle à la concentration du métal.

REFERENCES

1. K. H. Pool, *J. Polarog. Soc.*, 1967, **13,** 23.
2. A. Ciana and C. Furlani, *Electrochim. Acta*, 1965, **10,** 1149; C. Furlani, L. Sestili, A. Ciana and F. Garbassi, *ibid.*, 1967, **12,** 1393; 1970, **15,** 225.
3. V. Gutman, *Coordination Chemistry in Non-Aqueous Solutions*, p. 19. Springer Verlag, Vienna, 1968.
4. J. F. Coetzee, G. P. Cunningham, D. K. McGuire and G. P. Padmanabhan, *Anal. Chem.*, 1962, **34,** 1139.
5. D. F. Evans, C. Zawoyski and R. L. Kay, *J. Phys. Chem.*, 1965, **69,** 3878.
6. G. Kortüm, S. D. Gokhale and H. Wilski, *Z. Physik. Chem. (Frankfurt)*, 1955, **4,** 86.
7. G. A. Forcier and J. W. Olver, *Electrochim. Acta*, 1969, **14,** 135.
8. I. Y. Ahmed and C. D. Schmulbach, *J. Phys. Chem.*, 1967, **17,** 2358.
9. D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, 1951, **73,** 5321.
10. J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, Hasse, Copenhagen, 1957.
11. I. M. Kolthoff and J. J. Lingane, *Polarography*, Vol. 1, p. 211. Interscience, New York, 1952.
12. H. Matsuda, Y. Ayabe and K. Adachi, *Z. Elektrochem.*, 1963, **67,** 593.
13. H-S. Hsiung, *Thesis*, University of Cincinnati., *Univ. Microfilms* 60-6444, *Diss. Abstr.*, 1960, **21,** 3629.

Talanta, 1972, Vol. 19, pp. 559 to 565. Pergamon Press. Printed in Northern Ireland

USE OF LIGAND BUFFERS FOR IMPROVED SELECTIVITY IN THE POLAROGRAPHIC DETERMINATION OF METALS

POLAROGRAPHIC DETERMINATION OF ZINC IN THE PRESENCE OF A LARGE AMOUNT OF CADMIUM

GENKICHI NAKAGAWA
Laboratory of Analytical Chemistry, Nagoya Institute of Technology,
Showa-ku, Nagoya, Japan

MOTOHARU TANAKA
Laboratory of Analytical Chemistry, Faculty of Science,
Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received* 7 *June* 1971. *Accepted* 1 *August* 1971)

Summary—The use of ligand buffers composed of a chelating agent and an excess of polarographically inert metal is recommended for the selective polarographic determination of a metal in the presence of a second metal, which has a polarographic wave at a less negative potential than the metal to be determined. Theoretical considerations on the optimum ligand concentration and the optimum composition of the ligand buffer are followed by the determination of zinc in cadmium as an example.

IN THE POLAROGRAPHIC determination of a metal M_I, difficulties are encountered in the presence of a large amount of a second metal M_{II}, which gives a polarographic wave at a more positive potential. In such a case, one can avoid the interference of M_{II} by utilizing a ligand L which forms more or less stable complexes with M_{II}. In the presence of such a masking agent, the wave of M_{II} either diminishes or moves to a more negative potential.[1] However, this method cannot be useful when the ligand L affects the polarographic wave of M_I: if the ligand L forms complexes with M_I, the half-wave potential of M_I moves to a more negative potential and sometimes the diffusion current of M_I diminishes.

In this paper, the use of ligand buffers composed of a chelating agent and an excess of inert metal M_{III} is recommended for the selective polarographic determination of M_I in the presence of a second metal M_{II}. The determination of zinc in cadmium will be given as an example.

THEORETICAL CONSIDERATIONS

Suppose that a chelating agent L forms complexes with metals M_I and M_{II} and that the complexes M_IL and $M_{II}L$ do not give polarographic waves at the potentials where M_I and/or M_{II} give polarographic waves. In order to mask only the M_{II} wave by the chelating agent L, the conditional formation constant of $M_{II}L$, $K_{M_{II}'L}$, should be larger than that for M_IL, $K_{M_I'L}$. When an excess of the ligand L is added to a solution containing M_I and M_{II}, the wave of M_{II} is masked and, the excess of L forming M_IL_I with M_I, the wave-height of M_I diminishes too. However the determination of M_I would be possible, if one could find a third metal M_{III},* for which

---

* M_{III} should not interfere with the polarographic wave of M_I.

$K_{M_{II}'L} > K_{M_{III}'L} > K_{M_I'L}$: in the presence of an excess of M_{III} (ligand buffer[2] of L with an excess of M_{III}), the excess of ligand L forms $M_{III}L$ and liberates M_I from M_IL.

Optimum ligand concentration

The total concentrations of metals M_I and M_{II} are denoted as C_{M_I} and $C_{M_{II}}$ respectively. $[M_I']$ and $[M_{II}']$ refer to the total concentrations of M_I and M_{II} not combined with L. From the conditional formation constant of M_IL, $K_{M_I'L}$, we have

$$\frac{[M_IL]}{[M_I']} = K_{M_I'L}[L] \qquad (1)$$

The wave-height of M_I being proportional to $[M_I']$, $[M_IL]$ should not exceed 1% of C_{M_I} for successful quantitative polarographic determination of M_I: $[M_IL]/[M_I']$ should be smaller than 10^{-2}. Then from equation (1), we have

$$K_{M_I'L}[L] \leqslant 10^{-2}$$

or

$$[L] \leqslant 10^{-2}/K_{M_I'L} \qquad (2)$$

Now we consider the masking of M_{II}. From the conditional formation constant of $M_{II}L$, $K_{M_{II}'L}$, we have

$$\frac{[M_{II}L]}{[M_{II}']} = K_{M_{II}'L}[L] \qquad (3)$$

Thus in order to mask M_{II} as completely as possible, most of M_{II} should be in the form of $M_{II}L$: $[M_{II}L]/[M_{II}']$ or $K_{M_{II}'L}[L]$ should be sufficiently high. It should be noted, however, that the upper limit of [L] is given by equation (2).

Substitution of equation (2) into (3) yields

$$\frac{[M_{II}L]}{[M_{II}']} \leqslant \frac{K_{M_{II}'L}}{10^2 K_{M_I'L}} \qquad (4)$$

From equation (4) we realize that $K_{M_{II}'L}/K_{M_I'L}$ should be sufficiently large if a large amount of M_{II} is to be masked: when $K_{M_{II}'L}/K_{M_I'L} = 10^4$, the wave-height of M_{II} diminishes by a factor of 100 at the ligand concentration [L] given by equation (2′), whereas the decrease in the wave-height of M_I is only 1% of C_{M_I} at the same ligand concentration.

$$[L] = 10^{-2}/K_{M_I'L} \qquad (2')$$

Even though the wave-height of a second metal M_{II} (which is supposed to give rise to a wave at a potential less negative than that of M_I) attains several times that of M_I, the presence of the metal M_{II} does not make any difficulty in the polarographic determination of the metal M_I. Therefore when the condition $K_{M_{II}'L}/K_{M_I'L} = 10^4$ can be realized, the polarographic determination of M_I is possible in the presence of several hundred times as high a concentration of M_{II} as that of M_I.

Optimum composition of the ligand buffer[2]

The metal M_{III} to be added as a component of the ligand buffer for masking the metal M_{II} should not interfere with the polarographic wave of the metal M_I and should satisfy the condition: $K_{M_{II}'L} > K_{M_{III}'L} > K_{M_I'L}$. The optimum concentration of M_{III} is calculated as follows.

Denoting by C_L and $C_{M_{III}}$ the total concentrations of the added chelating agent L and the metal M_{III} respectively, we have

$$C_L = [M_IL] + [M_{II}L] + [M_{III}L] + [L'] \tag{5}$$

In equation (5) $[M_IL]$ and $[L']$ are very small in the presence of excess of M_{III} and can be neglected. Moreover, when masking of M_{II} is complete, $[M_{II}L]$ can be regarded as $C_{M_{II}}$. Then from equation (5) we have

$$[M_{III}L] = C_L - C_{M_{II}} \tag{5'}$$

From equation (5′) and the conditional formation constant of $M_{III}L$, $K_{M'_{III}L}$, we get

$$C_{M_{III}} = (C_L - C_{M_{II}})\left(1 + \frac{1}{[L]K_{M'_{III}L}}\right) \tag{6}$$

where [L] should be fixed at an optimum value as determined in the preceding section. Then the favourable value of $C_{M_{III}}$ is found from equation (6) for given values of C_L and $C_{M_{II}}$.*

DETERMINATION OF ZINC IN THE PRESENCE OF CADIUM

Cadmium and zinc give rise to a well-defined polarographic wave in NH_3–NH_4Cl supporting electrolyte. The half-wave potential of the former in this solution is about −0·8 V and that of the latter is about −1·3 V *vs*. SCE. Thus it is not difficult to determine cadmium in the presence of a large amount of zinc, but a large amount of cadmium makes difficult the polarographic determination of zinc. The formation constants of EGTA [ethyleneglycol-*bis*(2-aminoethyl ether)-*N*,*N*,*N′*,*N′*-tetra-acetic acid] complexes of cadmium and zinc are:[3] $K_{CdL} = 10^{16\cdot7}$ and $K_{ZnL} = 10^{14\cdot5}$. The difference of these two constants is larger than that of the corresponding EDTA complexes. Thus EGTA was chosen for the selective masking of cadmium in the presence of zinc.

In Fig. 1, logarithmic conditional formation constants $\log K_{M'L}$ are plotted for cadmium, zinc, calcium and barium as a function of $\log [NH_3]$.† As calcium and barium do not form ammine complexes, we can realise the following condition for a certain favourable value of $[NH_3]$: $K_{Cd'L} > K_{Ba'L}(K_{Ca'L}) > K_{Zn'L}$.

In Fig. 2 are given polarograms of cadmium and zinc in NH_3–NH_4Cl supporting electrolyte with and without added EGTA. In the presence of EGTA the cadmium wave disappears and the zinc wave-height diminishes.

---

* When masking of M_{II} is not quantitative and $C_{M_{II}}$ cannot be regarded as $[M_{II}L]$, (5′) is rewritten as:

$$C_L = [M_{II}L] + [M_{III}L]$$

Then from this equation and the conditional formation constants of $M_{II}L$ and $M_{III}L$, we have

$$C_{M_{III}} = \left\{C_L - C_{M_{II}}\left(\frac{[L]K_{M_{II}'L}}{1 + [L]K_{M_{II}'L}}\right)\right\}\left(\frac{1 + [L]K_{M'_{III}L}}{[L]K_{M'_{III}L}}\right)$$

for the favourable value of $C_{M_{III}}$ in the selective determination of M_I in the presence of M_{II}.

† We know of the formation of such a mixed ligand complex as $ZnLNH_3$ for L = EDTA. Though in this case also such mixed ligand complexes are expected, they are not taken into consideration, because we have no available data for their formation constants. The stepwise formation constants used to calculate the conditional formation constants are $\log K_1 = 2{\cdot}37$, $\log K_2 = 2{\cdot}44$, $\log K_3 = 2{\cdot}50$ and $\log K_4 = 2{\cdot}15$ for zinc ammine complexes, and $\log K_1 = 2{\cdot}65$, $\log K_2 = 2{\cdot}10$, $\log K_3 = 1{\cdot}44$ and $\log K_4 = 0{\cdot}93$ for cadmium ammines.

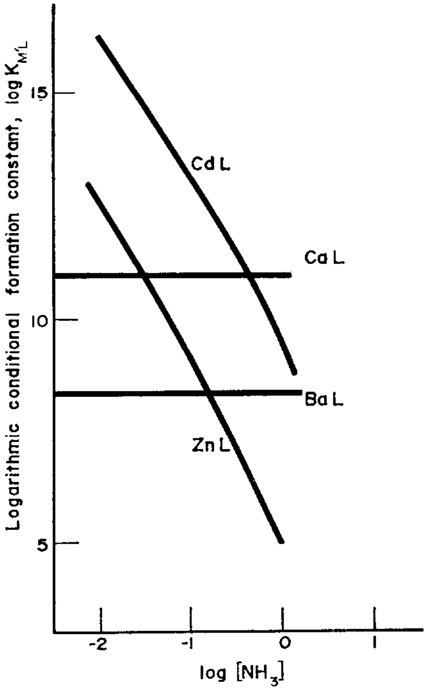


FIG. 1.—Logarithmic conditional formation constants of EGTA complexes of cadmium, zinc, calcium and barium as a function of log [NH$_3$].

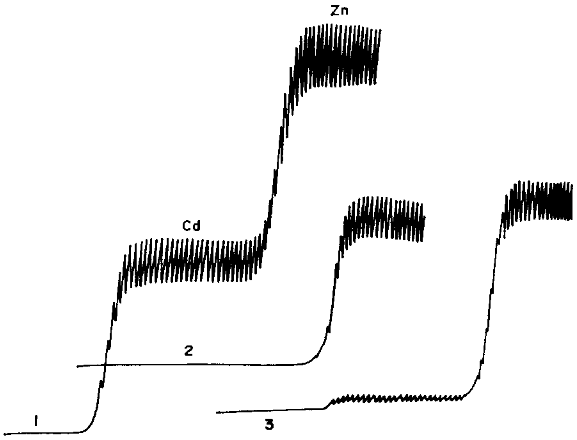


FIG. 2.—Polarograms of cadmium and zinc.

(1) Cd: 0·9 × $10^{-3}M$; Zn: 1 × $10^{-3}M$ in 0·5M NH_3–0·1M NH_4Cl and 0·01% gelatine.

(2) Solution (1) + 1·3 × $10^{-3}M$ EGTA.

(3) Solution (2) + 2 × $10^{-3}M$ $BaCl_2$.

Log $K_{Zn'L}$ being 6·2 in 0·5M NH_3 (Fig. 1), [L] should be smaller than $10^{-8 \cdot 2}$ in order to avoid diminution of the zinc wave in the presence of EGTA. Then we consider the masking of cadmium for $[L] = 10^{-8 \cdot 2}$. Log $K_{Cd'L}$ being 10·6 in 0·5M NH_3 (Fig. 1), we have immediately from equation (3): $[CdL]/[Cd'] = 10^{2 \cdot 4}$. Thus cadmium would be completely masked in this medium. As a metal to be added as a component of ligand buffer, barium is suitable, because $K_{Ba'L} = 10^{8 \cdot 4}$ (Fig. 1).* When barium is added in twice as much as the excess amount of EGTA ($[Ba^{2+}] = [BaL]$), $[L] = 10^{-8 \cdot 4}$ (see Ref. 2 for details).

Table I summarizes the wave-heights of zinc and cadmium in 0·5M NH_3–NH_4Cl

TABLE I.—DIFFUSION CURRENT OF ZINC AND CADMIUM

C_{EGTA}/C_{Cd}	$C_{Ba}/(C_{EGTA} - C_{Cd})$	i_d(Cd), μA	i_d(Zn), μA
0	0	6·24	6·03
1·1	0	0	3·54
1·1	2	0·18	5·62
1·1	5	0·36	6·07
1·1	10	0·60	6·05
1·2	2	0·12	5·78
1·2	5	0·30	6·03
1·2	10	0·63	6·02
1·3	2	0·22	5·95
1·3	5	0·42	6·04
1·3	10	0·66	6·06

$C_{Cd} = 1 \cdot 0 \times 10^{-3}M$; $C_{Zn} = 1 \cdot 0 \times 10^{-3}M$; $C_{EGTA} = 1 \cdot 1$–$1 \cdot 3 \times 10^{-3}M$; $C_{Ba} = 2$–$30 \times 10^{-4}M$; 0·5M NH_3–0·1M NH_4Cl; 0·01% gelatine.

containing EGTA and $BaCl_2$ in different proportions. When $C_{Ba}/(C_{EGTA} - C_{Cd})$ is 2, the wave-height of zinc is a little too low, while the recovery of zinc is quantitative for $C_{Ba}/(C_{EGTA} - C_{Cd}) \geqslant 5$. Under these conditions the wave-height of cadmium diminishes to between 1/10 and 1/20 of its normal value.

Figure 3 demonstrates the good linearity of the wave-height of zinc plotted *vs.* zinc concentration under the following conditions: $C_{Cd} = 5 \times 10^{-3}M$; $C_{Zn} = 0 \cdot 1$–$1 \times 10^{-3}M$; $C_{EGTA} = 5 \cdot 5 \times 10^{-3}M$ and $C_{Ba} = 5 \times 10^{-3}M$. In the same figure, the wave-height of cadmium is given as a broken line. Thus by the present method we can determine zinc in the presence of cadmium in concentrations 10–50 times that of the zinc.

Experiments revealed that the masking of cadmium was less complete than expected from the equilibrium considerations, and that a concentration of barium higher than calculated was necessary to realize a quantitative wave-height for zinc. This is because dissociations such as

$$CdL^{2-} + 4NH_3 \rightarrow Cd(NH_3)_4^{2+} + L^{2-}$$

would proceed at the electrode surface and some *kinetic* nature would be involved in the cadmium wave. The free ligand produced at the electrode surface suppresses the

---

* For 0·1M NH_3 a ligand buffer containing excess of calcium can be used for our purpose. However, the conditional formation constant being proportional to about the fourth power of $[NH_3]$, the concentration of ammonia should strictly be adjusted in the ligand buffer with excess of calcium. Thus we prefer the ligand buffer with excess of barium, for which the optimum concentration of ammonia is higher (0·5M) and easily kept constant.

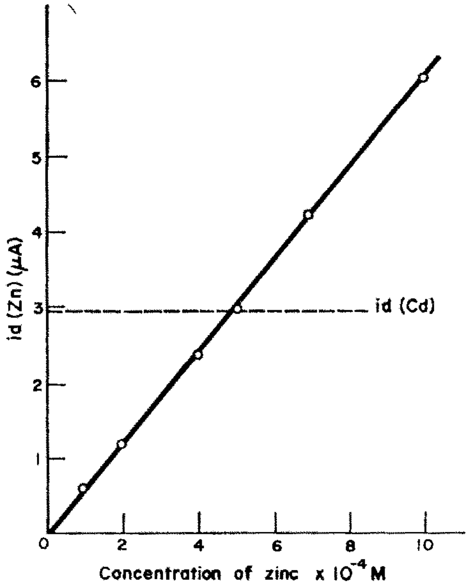


FIG. 3.—Wave-height of zinc as a function of zinc concentration.
$C_{Cd} = 5 \times 10^{-3}M$; $C_{Zn} = 0{\cdot}1\text{–}1 \times 10^{-3}M$; $0{\cdot}5M$ NH_3–$0{\cdot}1M$ NH_4Cl; $C_{EGTA} = 5{\cdot}5 \times 10^{-3}M$ and $C_{Ba} = 5 \times 10^{-3}M$.
Broken line indicates the wave height of cadmium under the same conditions.

zinc wave. Thus it is necessary to use a higher concentration of barium than calculated for the quantitative recovery of zinc.

Of metals giving rise to polarographic waves in ammoniacal solution, copper gives a wave at a more positive potential and the other metals such as nickel and cobalt do not give polarographic wave in the ammonia–EGTA supporting electrolyte. Therefore these metals do not interfere in the present method.

The use of ligand buffers can solve many problems in polarographic analysis, for example, polarographic determinations of cadmium in indium and lead in bismuth.

Cadmium and indium give polarographic waves at the same potential in many supporting electrolytes. In EDTA–Th ligand buffer, the indium wave disappears, while the cadmium wave is not affected and can be determined.

Bismuth gives a wave at a potential a little more positive than that of lead. The ligand buffer EDTA–Th masks the bismuth wave, while the lead wave remains unchanged ($\log K_{Bi'Y} > \log K_{Th'Y} > \log K_{Pb'Y}$). The method would thus be applicable to the determination of lead in crude copper after separation of bismuth and lead from copper by co-precipitation with ferric hydroxide.

EXPERIMENTAL

Reagents

EGTA solution, 0·10. Ten ml of $1M$ sodium hydroxide are added to 3·804 g of the pure reagent, and the whole is diluted to 100 ml.

Cadmium solution, $0{\cdot}01M$. Metallic cadmium (99·99%, 0·562 g) is dissolved in a small amount of hydrochloric acid. The excess of acid is expelled by evaporation and the solution is diluted to 500 ml.

Zinc solution, $0{\cdot}01M$. Metallic zinc (0·327 g) is dissolved in a small amount of hydrochloric acid and the same procedure is followed as for the cadmium solution.

Barium solution, 0·10*M*. Reagent grade $BaCl_2 \cdot 2H_2O$ (2·44 g) is dissolved in 100 ml of distilled water. The solution is standardized by EDTA titration.

Recommended procedure

In a 50-ml measuring flask take a 10-ml sample containing 20–25 mg of cadmium and 0·3–5 mg of zinc. Add 5 ml of 5*M* NH_3–1*M* NH_4Cl supporting electrolyte, and 3 ml of $10^{-1}M$ EGTA solution, 5 ml of $10^{-1}M$ $BaCl_2$ solution and 5 ml of 0·1% gelatine solution. Then dilute to the mark (the optimum barium concentration is 5–10 times the concentration of excess of EGTA). Take an aliquot of the solution in a polarographic cell and remove the dissolved oxygen with nitrogen gas which has passed through 0·5*M* ammonia solution. Record the polarogram from −0·5 to −1·5 V.

Zusammenfassung—Die Verwendung von Ligandenpuffern aus einem Chelatbildner und einem Überschuß von polarographisch inaktivem Metall wird vorgeschlagen für die selektive polarographische Bestimmung eines Metalls in Gegenwart eines zweiten Metalls, das eine polarographische Stufe bei einem weniger negativen Potential besitzt als das zu bestimmende Metall. Theoretische Erwägungen über die optimale Ligandenkonzentration werden angestellt sowie die Bestimmung von Zink in Cadmium als Beispiel ausgeführt.

Résumé—On recommande l'emploi de tampons à base de ligand, composés d'un agent chélatant et d'un excès d'un métal polarographiquement inerte, pour le dosage polarographique sélectif d'un métal en la présence d'un second métal qui a une vague polarographique à un potentiel moins négatif que le métal à doser. Des considérations théoriques sur la concentration optimale du ligand et la composition optimale du tampon à base de ligand sont suivies par le dosage du zinc dans le cadmium en tant qu'exemples.

REFERENCES

1. I. M. Kolthoff and J. J. Lingane, *Polarography*, 2nd Ed., Vol. 1, Interscience, New York (1952).
2. M. Tanaka, *Anal. Chim. Acta*, 1963, **29**, 193. See also *Anal. Chim. Acta*, 1965, **32**, 123 for the buffer capacity of ligand buffers.
3. L. G. Sillén and A. E. Martell (Eds.), *Stability Constants of Metal-Ion Complexes*. 2nd Ed., Chemical Society, London, 1964.

Talanta, 1972, Vol. 19, pp. 567 to 569. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Flow method in high-resolution nuclear magnetic resonance

(*Received* 7 *June* 1971. *Accepted* 2 *September* 1971)

RAPID CHEMICAL EXCHANGES have been studied by the variation in nuclear magnetic resonance (NMR) line shape, whereas slow reactions have been examined by the integration of NMR spectra. No paper has appeared on a device to follow reactions with a half-life in the range 1–10^3 sec, although low-resolution NMR flow-cells have been examined by many investigators.[1–7] The present paper deals with designs of flow-cells and their application in the observation of labile intermediates such as the yellow thiol forms of thiamine and monoethyl carbonate in alkaline solutions.

EXPERIMENTAL

A Varian A-60A spectrometer with a room-temperature probe was used. Five types of flow-cell were examined: (*A*) a straight glass tube, 1·6 mm bore, (*B*) a pipette-type tube, 1 and 3 mm bore, (*C*) a spiral capillary, 1 mm bore, in a conventional sample tube, 4·25 mm bore, with carbon tetrachloride, (*D*) a jet in the base of a conventional tube, (*E*) the conventional spinning tube with an inlet at the base and an outlet at a height of about 50 mm. Samples were fed from 100-ml syringes through plastic tube to the inlet. A glass Y-tube or a conventional jet mixing chamber was used to mix two kinds of fluid.

An ultraviolet spectrum of the yellow thiol form of thiamine was measured with a Perkin–Elmer 450 spectrometer in a 1-mm flow-cell at 8 sec after mixing 1m*M* thiamine hydrochloride and 1*M* sodium hydroxide in equal proportions. The molar absorptivities were $8{\cdot}5 \times 10^2$ l.mole.$^{-1}$ mm^{-1} at λ_{max} 335 nm, $1{\cdot}3 \times 10^3$ at 245 nm (shoulder) and $1{\cdot}6 \times 10^3$ at 230 nm. On the flow being stopped, the absorbance at 335 nm decreased at a rate of $8{\cdot}8 \times 10^{-4}$ sec^{-1} at 23° to form the colourless thiol (λ_{max} 235 and 263 nm).

RESULTS

Test of the flow-cells

The best results were obtained with flow-cell (*E*). The half-height width (*W*) of the methyl triplet in ethanol increased slightly from 1 to 1·5 Hz at a flow-rate of 3 ml/min. The peak height (*h*) and the intensity of the integrated curve (*i*) decreased rapidly with increase in the field (H_1). The values of *h* and *i* in the flow system were smaller than those in the stopped-flow system at low H_1 whereas the values at higher H_1 were nearly equal. The inhomogeneities of the static field (ΔH_0) in the directions of the flow (*y*) and the plane of spinning (*xz*) were averaged by the movements of the sample.

The resolution and intensities in cells *A*–*D* (without spinning) were decreased by the flow: *W* by 2–7 Hz, *h* by 1/10 and *i* by 1/5 at $H_1 = 0{\cdot}02$ mG. The circular flow in cells *C* and *D* was not sufficient to average ΔH_0 in the plane.

Labile intermediate in reaction of thiamine with alkali

It has been established from the ultraviolet absorption spectrum that the thiazolium form of thiamine (I) is converted by alkali into the colourless thiol form (III) *via* the pseudo-base and the yellow thiol form (II). Conventional NMR[9] gave a spectrum of a mixture of the colourless and yellow thiols for an alkaline solution of thiamine. Flow NMR with cell *E* was successfully applied to this reaction.

A yellow mixture of 1*M* thiamine hydrochloride and 4*M* potassium hydroxide at 5 sec after mixing gave an NMR spectrum corresponding to the pure yellow thiol. When the flow was stopped, the colourless thiol was formed at the expense of the yellow thiol form. The first-order rate constant of the reaction was estimated to be $1{\cdot}7 \times 10^{-3}$ sec^{-1} at 38°.

The structure of the yellow thiol form (II) proposed by Maier[8] is in accord with the chemical shifts. The peaks due to the protons on the thiazolium ring shift upfield during the reaction, whereas the peaks due to the protons on the pyrimidine ring remain almost constant. These shifts correspond to the change of a quaternary nitrogen atom (I) into a tertiary nitrogen atom (II and III).

Alkaline hydrolyses of ethoxacarbonyl compounds

When a mixture (1:1) of 1*M* urethane and 1*M* potassium hydroxide was flowing through the cell, only the NMR spectrum of urethane (τ: 8·78*t*, 5·92*q*) was observed. On stoppage of the flow, ethanol (τ: 8·84*t*, 6·36*q*) was formed from the urethane. The rate constant was $1{\cdot}6 \times 10^{-4}$ sec^{-1} at 38°.

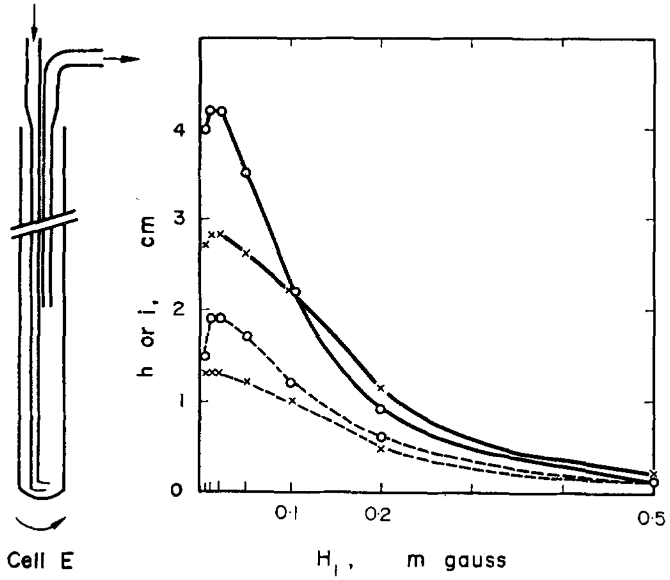


FIG. 1.—Dependence of the peak height (*h*, ———) and the integrated height (*i*, - - -) for the methyl triplet of ethanol on the radiofrequency field (H_1). ×, in flow-cell *E* at a flow-rate of 3 ml/min; ○, without flow.

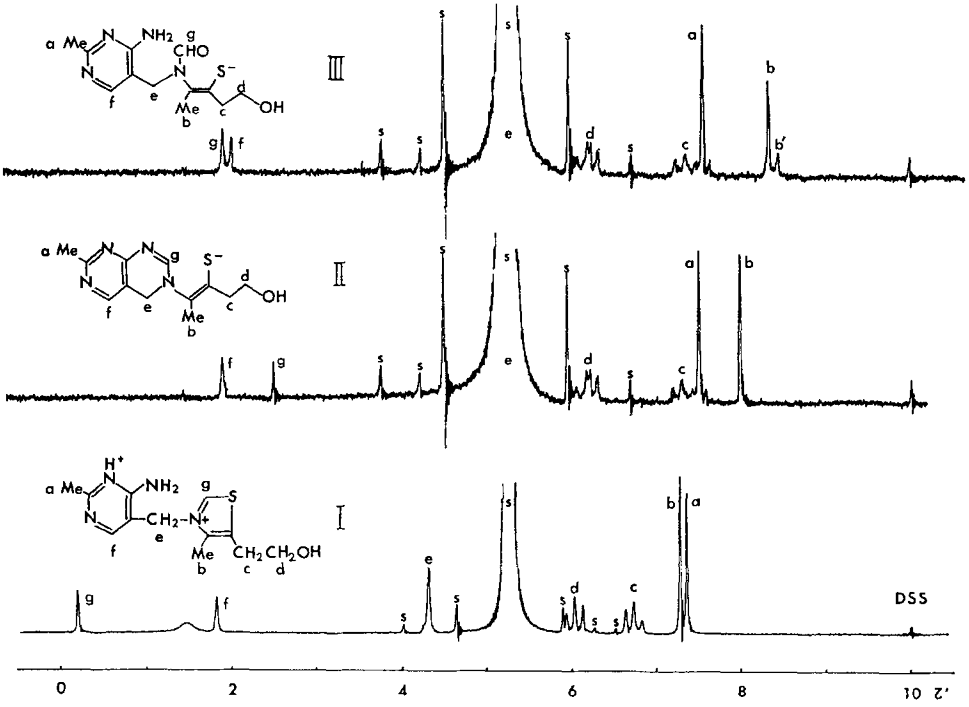


FIG. 2.—60-MHz NMR spectra of 1*M* thiamine hydrochloride (I) flowing in the cell *E*, the yellow thiol form (II) at 5 sec after mixing (I) with 4*M* KOH (1:1), and the colourless thiol form (III) at 20 min after the flow has stopped. *s*—solvent (water); *b*′—rotational isomer, 23%; DSS—sodium 2,3-dimethyl-2-silapentane-5-sulphonate as internal standard.

Any intermediate such as monoethyl carbonate or the complex of urethane with hydroxide ions was not observed. In the course of the alkaline hydrolysis of diethyl carbonate (τ: 8·74*t*, 5·80*q*) to ethanol, monoethyl carbonate (τ: 8·8*t*, 6·06*q*) was obtained as an intermediate.

DISCUSSION

Moderately rapid reactions with a half-life of 1–10^3 sec can be studied by high-resolution NMR spectroscopy, using the flow-cell *E*. A large flow-rate is necessary. To obtain the maximum signal from a flowing liquid, it is necessary to work at a relatively high field (H_1), which results in a broadening of the peaks. Saturation with increasing H_1 in the non-flow system was more rapid than that in the flow system, where rates of relaxation are comparable with the flow rate. The conventional instrument takes about 5 min to cover the range of 10 ppm and so requires large amounts of sample. Fourier NMR is expected to reduce this amount and decrease the time.

Zhernovoi[4] has studied a flow-through probe consisting of 2 successive coils in a static field, using broad-line NMR ($W = 60$–120 Hz). In such a flow probe for high-resolution NMR, reaction of prepolarized molecules in the first coil will be followed by depolarization in the second coil.

Acknowledgement—The authors thank Dr. S. Tatsuoka for permission to publish this work.

Chemical Research Laboratories
Research and Development Division
Takeda Chemical Ind., Ltd.
Osaka, Japan

Yutaka Asahi
Eiji Mizuta

Summary—Flow-cells have been designed for following moderately rapid reactions by high-resolution NMR. Labile intermediates such as the yellow thiol form of thiamine and monoethyl carbonate in alkaline solutions were detected by using this device.

Zusammenfassung—Es wurden Durchflußzellen entwickelt, um mäßig rasch verlaufende Reaktionen durch hochauflösende NMR zu verfolgen. Labile Zwischenprodukte wie die gelbe Thiolform von Thiamin und Monoäthylcarbonat in alkalischen Lösungen wurden mit Hilfe dieser Vorrichtung nachgewiesen.

Résumé—On a conçu des cellules à écoulement pour suivre les réactions modérément rapides par RMN à haute résolution. On a détecté avec ce dispositif des intermédiaires labiles tels que la forme thiol jaune de la thiamine et le monoéthylcarbonate en solutions alcalines.

REFERENCES

1. K. Schaumberg, *Dan. Kemi*, 1966, **47**, 177.
2. W. K. Genthe, *Dis. Abst.*, 1965, **26**, 3204.
3. A. Timur, *ibid.*, 1965, **26**, 3179.
4. A. I. Zhernovoi, *Isv. Akad. Nauk. USSR, Ser. Fiz.*, 1965, **29**, 311; 1963, **27**, 942, 945; *Chem. Abstr.*, 1965, **63**, 7915; 1965, **62**, 15612; 1963, **59**, 13506; 1962, **57**, 5738; 1962, **56**, 7083.
5. J. R. Singer, *J. Appl. Phys.*, 1960, **31**, 125.
6. A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, 1953, **90**, 358.
7. G. Saryan, *Proc. Indian Acad. Sci.*, 1951, **33A**, 107.
8. G. D. Maier and D. E. Metzler, *J. Am. Chem. Soc.*, 1957, **79**, 4386.
9. Y. Asahi, *Takeda Kenkyusho Nempo*, 1967, **26**, 15.

Talanta, 1972, Vol. 19, pp. 569 to 572. Pergamon Press. Printed in Northern Ireland

Application of urease to the precipitation of manganese(II) oxinate from homogeneous solution with urea in the presence of calcium

(*Received* 7 *June* 1971. *Accepted* 19 *June* 1971)

Since 1937 when Willard *et al.* proposed precipitation from homogeneous solution (PFHS) for the precipitation of aluminium hydroxide,[1] the method has been utilized for the gravimetric

Any intermediate such as monoethyl carbonate or the complex of urethane with hydroxide ions was not observed. In the course of the alkaline hydrolysis of diethyl carbonate (τ: 8·74*t*, 5·80*q*) to ethanol, monoethyl carbonate (τ: 8·8*t*, 6·06*q*) was obtained as an intermediate.

DISCUSSION

Moderately rapid reactions with a half-life of 1–10^3 sec can be studied by high-resolution NMR spectroscopy, using the flow-cell *E*. A large flow-rate is necessary. To obtain the maximum signal from a flowing liquid, it is necessary to work at a relatively high field (H_1), which results in a broadening of the peaks. Saturation with increasing H_1 in the non-flow system was more rapid than that in the flow system, where rates of relaxation are comparable with the flow rate. The conventional instrument takes about 5 min to cover the range of 10 ppm and so requires large amounts of sample. Fourier NMR is expected to reduce this amount and decrease the time.

Zhernovoi[4] has studied a flow-through probe consisting of 2 successive coils in a static field, using broad-line NMR (W = 60–120 Hz). In such a flow probe for high-resolution NMR, reaction of prepolarized molecules in the first coil will be followed by depolarization in the second coil.

Acknowledgement—The authors thank Dr. S. Tatsuoka for permission to publish this work.

Chemical Research Laboratories
Research and Development Division
Takeda Chemical Ind., Ltd.
Osaka, Japan

YUTAKA ASAHI
EIJI MIZUTA

Summary—Flow-cells have been designed for following moderately rapid reactions by high-resolution NMR. Labile intermediates such as the yellow thiol form of thiamine and monoethyl carbonate in alkaline solutions were detected by using this device.

Zusammenfassung—Es wurden Durchflußzellen entwickelt, um mäßig rasch verlaufende Reaktionen durch hochauflösende NMR zu verfolgen. Labile Zwischenprodukte wie die gelbe Thiolform von Thiamin und Monoäthylcarbonat in alkalischen Lösungen wurden mit Hilfe dieser Vorrichtung nachgewiesen.

Résumé—On a conçu des cellules à écoulement pour suivre les réactions modérément rapides par RMN à haute résolution. On a détecté avec ce dispositif des intermédiaires labiles tels que la forme thiol jaune de la thiamine et le monoéthylcarbonate en solutions alcalines.

REFERENCES

1. K. Schaumberg, *Dan. Kemi*, 1966, **47**, 177.
2. W. K. Genthe, *Dis. Abst.*, 1965, **26**, 3204.
3. A. Timur, *ibid.*, 1965, **26**, 3179.
4. A. I. Zhernovoi, *Isv. Akad. Nauk. USSR, Ser. Fiz.*, 1965, **29**, 311; 1963, **27**, 942, 945; *Chem. Abstr.*, 1965, **63**, 7915; 1965, **62**, 15612; 1963, **59**, 13506; 1962, **57**, 5738; 1962, **56**, 7083.
5. J. R. Singer, *J. Appl. Phys.*, 1960, **31**, 125.
6. A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, 1953, **90**, 358.
7. G. Saryan, *Proc. Indian Acad. Sci.*, 1951, **33A**, 107.
8. G. D. Maier and D. E. Metzler, *J. Am. Chem. Soc.*, 1957, **79**, 4386.
9. Y. Asahi, *Takeda Kenkyusho Nempo*, 1967, **26**, 15.

Talanta, 1972, Vol. 19, pp. 569 to 572. Pergamon Press. Printed in Northern Ireland

Application of urease to the precipitation of manganese(II) oxinate from homogeneous solution with urea in the presence of calcium

(*Received* 7 *June* 1971. *Accepted* 19 *June* 1971)

SINCE 1937 when Willard *et al.* proposed precipitation from homogeneous solution (PFHS) for the precipitation of aluminium hydroxide,[1] the method has been utilized for the gravimetric determination of many metallic and non-metallic ions. In the PFHS method, the hydrolysis of urea has often been applied to raise the pH of the solution. We have found that urease can be used in the hydrolysis of urea in the PFHS method and have applied it in the precipitation of nickel dimethylglyoximate[2] and of cobalt 8-hydroxyquinaldinate.[3] Although precipitation of manganese(II) oxinate had not been recommended as a gravimetric method, it has been found satisfactory.[4] In this study, it was found that rate of increase of pH depends on the amount and purity of urease used and the concentration of citric acid, *etc.*[4] The rate of pH increase can be regulated by changing the urease concentration if other experimental conditions are kept constant.

The pH ranges for precipitation of calcium and manganese oxinates are similar.[5,6] Therefore the effect of calcium on the precipitation of manganese(II) oxinate was investigated.

EXPERIMENTAL

Reagents

Manganese solution. A solution containing 0·25–3 g of manganese(II) per litre was prepared by dissolving manganese(II) sulphate in water. The manganese solution was standardized with EDTA solution which had been standardized with metallic zinc (99·999% pure), Eriochrome Black T being used as indicator.

Calcium solution. Aqueous solution, 1 mg/ml.

Ascorbic acid. Used as the dry powder.

Citric acid. Aqueous solution, 10%.

Urea. Aqueous solution, 20%.

Oxine. Ethanolic solution (2%) prepared immediately before use.

Urease. Aqueous solution (0·01%) prepared immediately before use (activity 8300 units/g, Sigma Chem. Co. Type VI).

All chemicals used were analytical-reagent grade.

Procedure

To a solution containing 24·46 mg of manganese(II) and 20 mg of calcium were added 100 mg of ascorbic acid, 1 ml of 10% citric acid solution, 50 ml of 20% urea solution, and 7 ml of 2% ethanolic oxine solution. The solution was diluted to *ca.* 200 ml and the pH was adjusted to 5·0 with ammonia solution. Four series of such solutions (eight solutions per series) were prepared and then urease was added: 0·6 mg (series *a*), 0·3 mg (series *b*), 0·2 mg (series *c*) and 0·1 mg (series *d*). These solutions were kept at 35°. After a measured time the pH of the solution was measured and the precipitate formed was filtered off, washed, dried and weighed.

RESULTS AND DISCUSSION

The effect of the urease concentration on the rate of pH increase is shown in Fig. 1. If the pH of the solution rises rapidly (Fig. 1*a*), the precipitates formed are similar to those produced by the

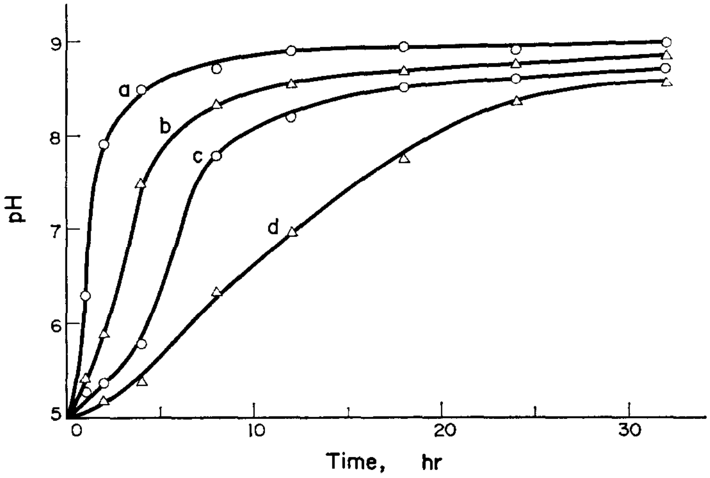


FIG. 1.—pH-time curves. *a*, urease 0·6 mg; *b*, urease 0·3 mg; *c*, urease 0·2 mg; *d*, urease 0·1 mg.

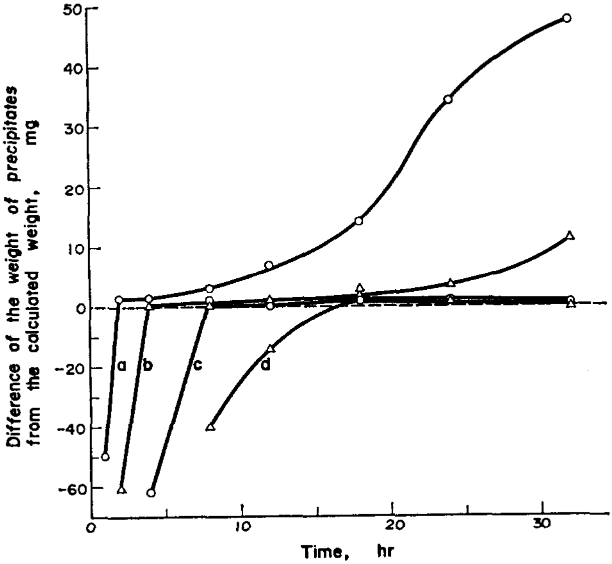


FIG. 2.—Effect of the reaction time on the formation of precipitates. (Expected weight of Mn(II) oxinate: 152·86 mg.)

ordinary method. When the pH takes 6–10 hr to reach a value of >8, satisfactory precipitates are obtained.

The weights of the precipitates are plotted against the reaction time in Fig. 2. The broken line in Fig. 2 shows the calculated weight of manganese(II) oxinate from the amounts of manganese taken. The amount of precipitate formed increases with reaction time. When the increase in pH is rapid, the weight of precipitate increases above the calculated value (Fig. 2*a*), but when the pH increases slowly, the weight excess is small (Fig. 2*b*–*d*).

Calcium in the precipitates

It was assumed that the increased weights of precipitates were due to calcium. To prove this, the precipitates were dissolved in dilute hydrochloric acid and the calcium contents were determined by atomic-absorption spectroscopy. The results are shown in Fig. 3.

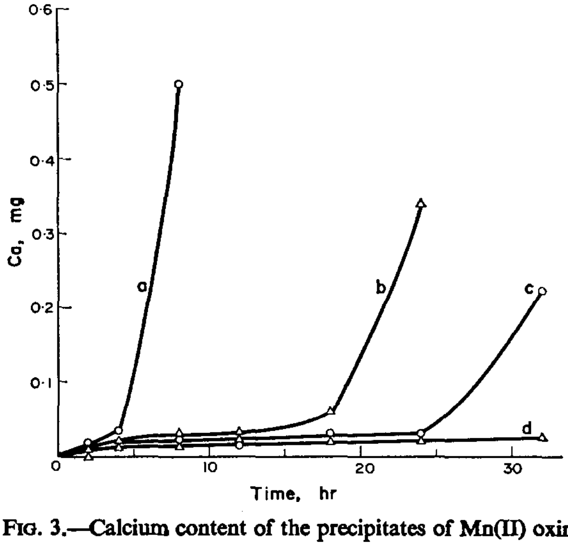


FIG. 3.—Calcium content of the precipitates of Mn(II) oxinate.

TABLE I.—DETERMINATION OF MANGANESE

		PFHS method		Conventional method	
Mn taken, *mg*	Ca taken, *mg*	Mn found, *mg*	Difference, *mg*	Mn found, *mg*	Difference, *mg*
19·38	5	19·39	+0·01	19·54	+0·16
19·38	10	19·42	+0·04	19·54	+0·07
19·38	20	19·41	+0·03	20·21	+0·83
19·38	40	19·42	+0·04	22·88	+3·50
22·91	60	23·06	+0·15	—	—
22·91	100	23·87	+0·16	—	—

When the pH of the solution rose rapidly (Fig. 3*a*), the calcium content in the precipitate increased rapidly with reaction time. However, when the pH rose more slowly, the calcium content of the precipitates stayed within limits comparable with the experimental error. The calcium contained in the precipitate increases rapidly at pH >8·5. This rapid increase in calcium content may be due to the precipitation of calcium carbonate. The presence of calcium carbonate may be proved by the fact that when the precipitate was dissolved in dilute hydrochloric acid, carbon dioxide was evolved. Carbon dioxide was generated by decomposition of urea and dissolved in the solution. When a solution of calcium containing urea was heated, calcium carbonate was precipitated at pH values over 8·5, and the weights of the precipitates increased rapidly at pH >8·5, which agrees with the literature values of the pH at which calcium carbonate is precipitated.

Determination of manganese(II) as oxinate in the presence of calcium

Manganese(II) was determined satisfactorily as the oxinate in the presence of calcium by the procedure given, using 0·3 mg of urease and keeping the mixed solution for 8 hr at 35°. The results are shown in Table I with the results obtained by the conventional wet method.[7]

Acknowledgement—The authors wish to acknowledge the partial assistance of the Ministry of Education, Japan, in supporting the investigation.

Department of Chemistry
Faculty of Science
Hokkaido University
Sapporo, Japan

SEIICHIRO HIKIME
HITOSHI YOSHIDA
MITSUHIKO TAGA
SHIGERU TAGUCHI

Summary—The effect of calcium on precipitation of manganese(II) oxinate from homogeneous solution by means of decomposition of urea with urease was investigated. Manganese was determined satisfactorily in the presence of calcium.

Zusammenfassung—Der Einfluß von Calcium auf die Fällung von Mangan(II)-oxinat aus homogener Lösung mittels Zersetzung von Harnstoff mit Urease wurde untersucht. Mangan ließ sich in Gegenwart von Calcium zufriedenstellend bestimmen.

Résumé—On a étudié l'influence du calcium sur la précipitation de l'oxinate de manganèse(II) d'une solution homogène au moyen de la décomposition de l'urée par l'uréase. On a dosé le manganèse de manière satisfaisante en la présence de calcium.

REFERENCES

1. H. H. Willard and N. K. Tang, *J. Am. Chem. Soc.*, 1937, **59**, 1190.
2. S. Hikime, H. Yoshida and M. Taga, *Talanta*, 1967, **14**, 1417.
3. M. Taga, H. Yoshida and S. Hikime, *Bunseki Kagaku*, 1968, **17**, 1252.
4. S. Taguchi, M. Taga, H. Yoshida and S. Hikime, *ibid.*, 1971, **20**, 570.
5. L. Erdey, *Gravimetric Analysis*, Vol. I, p. 211. Pergamon, Oxford, 1963.
6. H. Goto, *Nippon Kagaku Zasshi*, 1933, **54**, 725.
7. K. Motojima, *Shin Bunsekikagaku Koza, Kyoritsu Shuppan*, 1959, **6**, 46.

Talanta, 1972, Vol. 19, pp. 573 to 577. Pergamon Press. Printed in Northern Ireland

Qualitative analysis of ultraviolet-absorbing substances by use of fluorescent materials

(*Received* 7 *June* 1971. *Accepted* 23 *November* 1971)

THE SPECTRAL REGION to which the human eye responds is restricted to the narrow range of about 400–800 nm. Consequently, a great number of colour reactions have been developed for detection of colourless substances, and many new reactions are proposed every year. On the other hand, for detection of colourless substances absorbing ultraviolet light, use of fluorescent materials has been developed, and recently a mixed fluorescent material was proposed for detection of these substances as coloured compounds, and thus to increase the selectivity of detection.

USE OF FLUORESCENT MATERIALS FOR DETECTION OF ULTRAVIOLET-ABSORBING SUBSTANCES

Brockman and Volpers[1] were the first to separate colourless substances on adsorption columns impregnated with a fluorescent material. The adsorption zones appeared under monochromatic ultraviolet light as dark bands against a brilliant background. They used Morin, a pentahydroxyflavone, to make alumina fluoresce (300 mg per 500 g of alumina), berberine for silica gel, diphenylfluoridine sulphonic acid for calcium carbonate, and Morin for magnesium oxide. This method is applicable to those substances which absorb ultraviolet light in the wavelength region causing fluorescence.

Sease[2] described the use of silica gel mixed with 2·5 % of fluorescent zinc sulphide, and Brockmann[1] suggested its slight adsorptivity. The usable wavelength range was limited to 330–390 nm. Sease[3] extended the range to 230–390 nm by admixture with 2·5 % of fluorescent zinc silicate. On columns of the fluorescent silica gel he separated 40 binary mixtures involving 25 different compounds, and detected the zones by illuminating the columns with a hydrogen lamp which provides continuous ultraviolet light. With such a light-source, however, the detection limit for an individual compound should be higher than that with suitable monochromatic light.

Kirchner *et al.*[4] made fluorescent chromatostrips with a mixture of 19 g of adsorbent, 1 g of starch, 0·15 g of zinc silicate and 0·15 g of zinc cadmium sulphide, to separate and detect some unsaturated organic compounds. The technique has grown into thin-layer chromatography with fluorescent adsorbents, the most popular nowadays among these being Merck's Silica Gel F_{254} containing fluorescent zinc silicate.

Fluorescent materials have also been used to make fluorescent screens which are mainly useful for detecting spots of ultraviolet-absorbing substances on paper.

Although the combinations of some fluorescent materials mentioned above are usable for a wide wavelength range, they have poor selectivity since the substances appear as dark and uncoloured spots. In contrast, by the method described here, the substances show different colours, depending on their ultraviolet absorbing spectra, and thus the selectivity is much increased.

Light source

Various kinds of mercury lamps of different pressure have been used for the light source, in combination with suitable filters, the simplest and most popular among them being a low-pressure lamp which emits a strong line at 254 nm and some weak lines, and a fluorescent lamp which is made from a similar lamp coated with fluorescent barium metasilicate and emits a band spectrum around 350 nm.

Sease[3] used a hydrogen lamp to obtain an ultraviolet continuum. Tamura *et al.*[5] improved the low-pressure mercury lamp to supplement the energy of wavelength longer than 254 nm. Three kinds of fluorescent materials which absorb light at 254 nm and emit ultraviolet light of longer wavelength—$(Zn,Ca)_3(PO_4)_2/Tl$ (fluorescence maximum, 310 nm), $BaSi_2O_5/Pb$ (350 nm) and $(Ba,Sr,Mg)SiO_3{\cdot}SO_4/Pb$ (370 nm)—were mixed in the proportions 26·0, 33·2 and 40·8 % respectively; the mixture was bound with acetylcellulose to make a film which was placed behind the mercury lamp, and a Toshiba UV-D25 filter was attached in front of the lamp. The emission spectrum of the light source thus obtained is shown in Fig. 1.

Since the fluorescent film gradually deteriorates, the light source was further improved by coating half of the inner surface of the discharging tube with the same fluorescent mixture (Fig. 2).*

---

* The light source is to be manufactured by Tokyo Kogaku Kikai K.K.

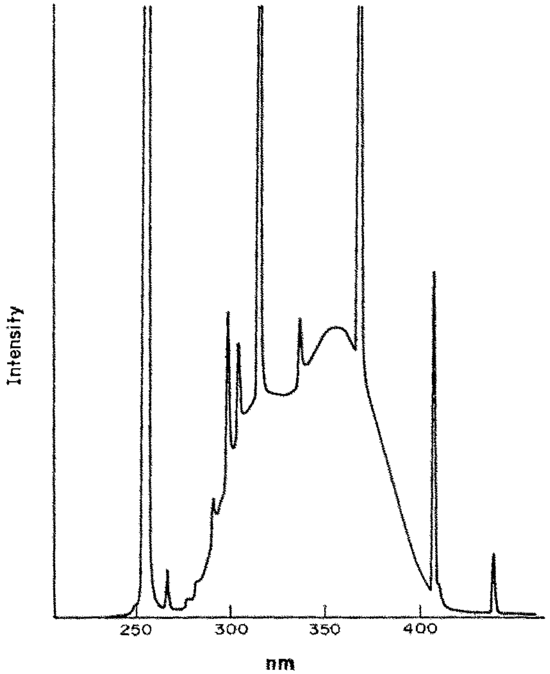


FIG. 1.—Emission spectrum of the light source (uncorrected).

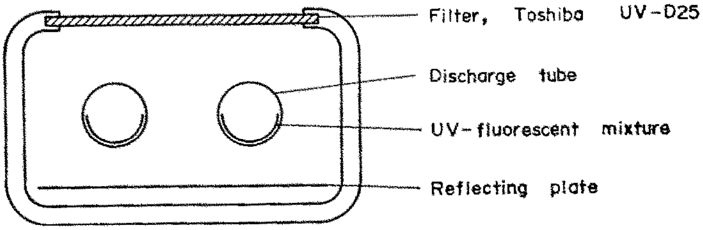


FIG. 2.—Cross-section of the light source.

Use of mixed fluorescent materials

Tamura *et al.*[5] selected three kinds of fluorescent materials which have different excitation spectra and fluorescent colours (blue, green and red) from the products of Tokyo Shibaura Electric Co. (Fig. 3), and mixed them so as to obtain white fluorescence on irradiation with continuous ultraviolet light (Fig. 3, Table I).

The mixed fluorescent materials display different colours according to the wavelengths of the irradiating ultraviolet light. The mixed fluorescent materials A and B change their colour from blue, through green, yellow and orange, to red on changing the excitation wavelength from 250 to 350 nm. Thus the visible spectrum seems to be transferred to the ultraviolet region.

Tamura *et al.* applied the mixed fluorescent material A to detection of ultraviolet absorbing substances as coloured substances.

Fluorescent screen. The mixed fluorescent material was mixed with an equal quantity of 1% starch solution and spread on a glass plate with an applicator, or mixed with several times its quantity of 5% acetylcellulose solution in acetone and spread on a polyvinyl chloride plate, to produce a fluorescent screen.*

* A fluorescent screen made from mixture A is commercially available under the name of Lumicolor-Plate (Wako Pure Chemical Industries, Ltd.).

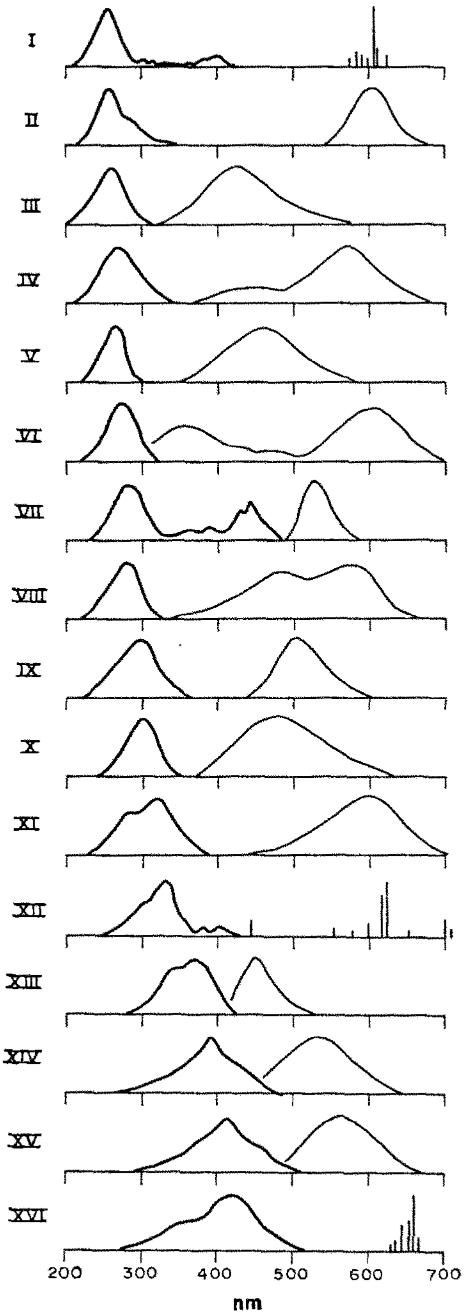


FIG. 3.—Spectra and fluorescent colours of inorganic fluorescent materials.

—— Excitation spectra (uncorrected); —— Emission spectra (uncorrected); I: Y_2O_3/Eu (SPD-374), red; II: $Cd_2B_2O_5$/Mn (SPD-6), orange-red; III: $CaWO_4$ (SPD-1B), blue-violet; IV: $3Sr_3(PO_4)_2\cdot SrF_2$/Mn, Sn (SPD-106), yellow; V: $Sr_2P_2O_7$/Sn (SPD-105), blue; VI: $CaSiO_3$/Pb, Mn (SPD-11B), orange; VII: Zn_2SiO_4/Mn (SPD-3B), green; VIII: $3Ca_3(PO_4)_2\cdot CaFCl$/Sb, Mn (SPD-1451), white; IX: $MgGa_2O_4$/Mn (SPD-4), green; X: $MgWO_4$ (SPD-2), blue-white; XI: $(SrMgBa)_3(PO_4)_2$/Sn (SPD-103A), orange; XII: YVO_4/Eu (SPD-373B), red; XIII: ZnS/Ag (SPD-351), blue; XIV: ZnCdS/Ag (SPD-363), green; XV: ZnCdS/Ag (SPD-315), yellow; XVI: $Mg_6(AsB)_2O_{11}$/Mn (SPD-102), red

TABLE I.—COMPOSITION OF SOME MIXED FLUORESCENT MATERIALS

Symbol	Component	Mixing ratio
A	V, VII, XII	20:5:1
B	V, VII, XVI	12:3:2
C	VII, XII, XIII	5:1:2
D	I, IX, XIII	3:5:1

After chromatographic or electrophoretic separation, the filter paper was placed on the light source and covered with the fluorescent screen. Then the ultraviolet-absorbing compounds were observed as coloured spots on the white background.

The colour of a spot corresponds to the absorption spectrum of the compounds in it, and vitamin C, which has an absorption maximum at 265 nm, gives a red spot on a chromatogram, as expected from the spectrum of A. In some cases, however, the colour does not correspond to the absorption spectrum in the solution, because of changes caused by adsorption or solidification, or because of overlap with the fluorescence of the compound as in the case of vitamin B_6. A colour change from red to brown during irradiation was observed in the case of vitamin B_1, and this was the result of photochemical decomposition. The limits of detection depend on the molar absorptivities of the compounds, and those of vitamin B_1, C and nicotinamide were found to be 0·1, 0·5, 0·5 and 0·4 μg respectively in chromatography with n-butanol, acetic acid and water (4:1:5 v/v; upper phase).

Gases and liquids are observed by placing them in a quartz cell and putting this between the light source and the fluorescent screen. The vapour of benzene then looks red and aromatic impurities in a solvent can be detectable.

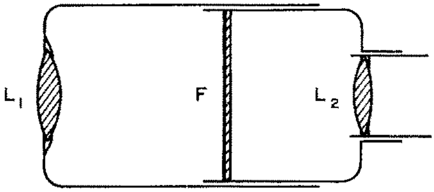


FIG. 4.—A viewer for ultraviolet-absorbing substances. L_1—quartz lens; F—fluorescent screen, L_2—glass lens.

A viewer for ultraviolet-absorbing substances has been developed, as shown in Fig. 4. An object is irradiated with the light source, the image is focused on the screen, and the fluorescent image is observed through the lens L_2.

Thin-layer and column chromatography. The fluorescent screen is scarcely applicable for thin-layer chromatography since ordinary adsorbents and glass absorb light of wavelength shorter than 300 nm, and therefore 5–10% of the mixed fluorescent material is added to the adsorbent.* The colour is better if observed from the back of the thin layer.

The detection limits on thin layers are generally lower than on paper, and 0·1 μg of vitamin B_1 and 0·3 μg of nicotinamide are sufficient for detection.

A similar fluorescent adsorbent in a quartz tube has been used for column chromatography, for example, an adsorbent was made by hydrolysis of ethyl silicate containing fluorescent material A, to achieve homogeneous distribution of the fluorescent components through the adsorbent.

Takitani *et al.* studied separation of hypnotics[6] and other drugs[7] on thin layers and columns of silica gel containing the mixed fluorescent material.

DISCUSSION

Strong acids or alkalis should not be applied to the mixed fluorescent material, for some of the components would be decomposed. Ultraviolet-absorbing solvents, if present, should be removed completely before the observation. The irradiation time should be kept as short as possible to avoid photochemical decomposition of unstable compounds.

* Silica gel containing the fluorescent material A, Wakogel B-5 UA is available (Wako Pure Chemical Industries, Ltd.).

Subject to these conditions, the mixed fluorescent material should be widely applicable not only to qualitative analysis of natural products, biological substances, drugs, synthetic materials *etc*, but also to their purification and for tracing their chemical reactions.

Acknowledgements—The author wishes to thank *Japan Analyst* for permission to reprint figures.

Faculty of Pharmaceutical Sciences
University of Tokyo, Tokyo, Japan
ZENZO TAMURA

Summary—Developments of detection techniques of ultraviolet absorbing substances with fluorescent materials are reviewed.

Zusammenfassung—Es wird eine Übersicht über Nachweisverfahren von Ultraviolett absorbierenden Substanzen mit Hilfe fluoreszenzfähiger Stoffe gegeben.

Résumé—On passe en revue les développements de techniques de détection de substances absorbant dans l'ultra-violet avec des produits fluorescents.

REFERENCES

1. H. Brockmann and F. Volpers, *Ber.*, 1947, **80**, 77.
2. J. W. Sease, *J. Am. Chem. Soc.*, 1947, **69**, 2242.
3. *Idem, ibid.*, 1947, **70**, 3630.
4. J. G. Kirchner, J. M. Miller and G. J. Keller, *Anal. Chem.*, 1951, **23**, 420.
5. Z. Tamura, C. Kim, N. Hosoda, S. Takitani, M. Suzuki, M. Suzuki and M. Inoue, *Bunseki Kagaku*, 1970, **19**, 518.
6. S. Takitani, *J. Hyg. Chem. Japan*, 1969, **15**, 13.
7. S. Takitani and M. Suzuki, *ibid.*, 1970, **16**, 86.

Talanta, 1972, Vol. 19, pp. 577 to 582. Pergamon Press. Printed in Northern Ireland

Automatic ion-exchange chromatograph for analysis of alkali and alkaline earth metal mixtures

(*Received* 7 *June* 1971. *Accepted* 28 *November* 1971)

FLAME PHOTOMETRY has been widely used for determination of alkali and alkaline earth metals, but a sample solution of several millilitres is necessary. A new method for ultramicro determination of these metals had been developed by the authors.[1–3] A hydrogen flame-ionization detector is used as sensor and the sample solution required for analysis is only several microlitres. This detector, in which an electric current is caused by ionization of the metals in the flame, has high sensitivity but lacks selectivity. Use of this detector with automatic ion-exchange chromatography on an inorganic ion-exchanger has been studied.

EXPERIMENTAL

Chromatograph

A block diagram of the automatic chromatograph is shown in Fig. 1 and some details in Fig. 2. The chromatograph consists of a hydrogen flame-ionization detector, an ion-exchange column, a motor-driven turntable, a photoelectric monitor, and a heater chamber to evaporate the eluate. The detector had double jets for two hydrogen flames (Fig. 3). Salts of alkali and alkaline earth metals were evaporated in the lower flame (the evaporating flame) and electrical responses corresponding to ionization of these metals were measured in the upper flame (the ionizing flame). The ion-exchange

Subject to these conditions, the mixed fluorescent material should be widely applicable not only to qualitative analysis of natural products, biological substances, drugs, synthetic materials *etc*, but also to their purification and for tracing their chemical reactions.

Acknowledgements—The author wishes to thank *Japan Analyst* for permission to reprint figures.

Faculty of Pharmaceutical Sciences
University of Tokyo, Tokyo, Japan

ZENZO TAMURA

Summary—Developments of detection techniques of ultraviolet absorbing substances with fluorescent materials are reviewed.

Zusammenfassung—Es wird eine Übersicht über Nachweisverfahren von Ultraviolett absorbierenden Substanzen mit Hilfe fluoreszenzfähiger Stoffe gegeben.

Résumé—On passe en revue les développements de techniques de détection de substances absorbant dans l'ultra-violet avec des produits fluorescents.

REFERENCES

1. H. Brockmann and F. Volpers, *Ber.*, 1947, **80**, 77.
2. J. W. Sease, *J. Am. Chem. Soc.*, 1947, **69**, 2242.
3. *Idem, ibid.*, 1947, **70**, 3630.
4. J. G. Kirchner, J. M. Miller and G. J. Keller, *Anal. Chem.*, 1951, **23**, 420.
5. Z. Tamura, C. Kim, N. Hosoda, S. Takitani, M. Suzuki, M. Suzuki and M. Inoue, *Bunseki Kagaku*, 1970, **19**, 518.
6. S. Takitani, *J. Hyg. Chem. Japan*, 1969, **15**, 13.
7. S. Takitani and M. Suzuki, *ibid.*, 1970, **16**, 86.

Talanta, 1972, Vol. 19, pp. 577 to 582. Pergamon Press. Printed in Northern Ireland

Automatic ion-exchange chromatograph for analysis of alkali and alkaline earth metal mixtures

(*Received* 7 *June* 1971. *Accepted* 28 *November* 1971)

FLAME PHOTOMETRY has been widely used for determination of alkali and alkaline earth metals, but a sample solution of several millilitres is necessary. A new method for ultramicro determination of these metals had been developed by the authors.[1–3] A hydrogen flame-ionization detector is used as sensor and the sample solution required for analysis is only several microlitres. This detector, in which an electric current is caused by ionization of the metals in the flame, has high sensitivity but lacks selectivity. Use of this detector with automatic ion-exchange chromatography on an inorganic ion-exchanger has been studied.

EXPERIMENTAL

Chromatograph

A block diagram of the automatic chromatograph is shown in Fig. 1 and some details in Fig. 2. The chromatograph consists of a hydrogen flame-ionization detector, an ion-exchange column, a motor-driven turntable, a photoelectric monitor, and a heater chamber to evaporate the eluate. The detector had double jets for two hydrogen flames (Fig. 3). Salts of alkali and alkaline earth metals were evaporated in the lower flame (the evaporating flame) and electrical responses corresponding to ionization of these metals were measured in the upper flame (the ionizing flame). The ion-exchange

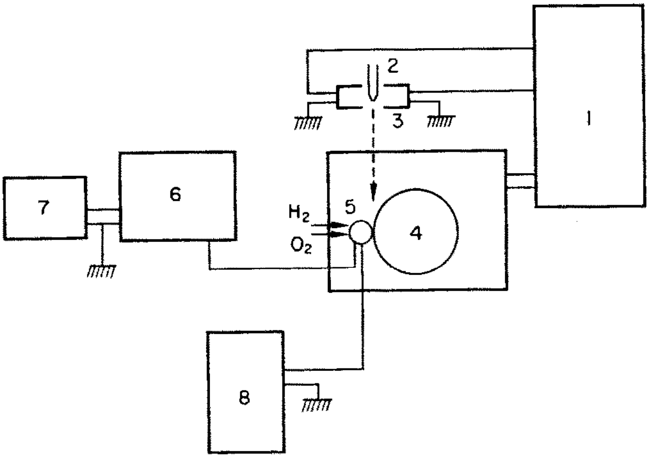


FIG. 1.—Schematic diagram of chromatograph. ① Control box; ② ion-exchange column; ③ device for monitoring a drop of eluate; ④ turntable (sample holders); ⑤ hydrogen flame-ionization detector; ⑥ d.c. amplifier; ⑦ recorder; ⑧ constant-voltage stabilizer.

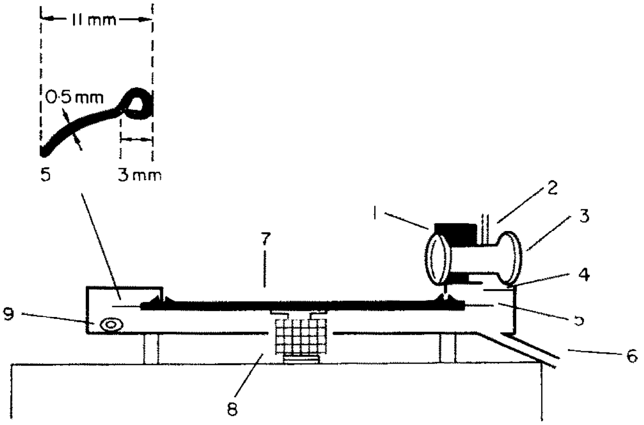


FIG. 2.—Vertical plane of chromatograph. ① Detector; ② ion-exchange column; ③ device for monitoring a drop of eluate; ④ shock absorber; ⑤ sample holder (Pt); ⑥ drain; ⑦ turntable (160 mm diameter); ⑧ screw for setting the height of sample holder; ⑨ heater for evaporating eluate.

column was a silica tube of 4·2 mm bore packed with zirconium phosphate (Bio-Rad, 100–200 mesh) to a height of 20 mm. The turntable had 47 platinum sample holders. A net or ring, made of fine platinum wire (0·1 mm diameter) was placed below the column to reduce the speed of a falling drop of effluent and ensure successful loading on a sample holder. The photoelectric monitor was the same as one used for a fraction collector. The heater chamber was set to evaporate eluates, especially those containing ammonium chloride, on the sample holders before they were inserted into the evaporating flame. Optimum temperatures of the heating zone are shown in Fig. 4. The chromatographic and sampling devices are shown in Fig. 5.

When a drop of effluent from the column is loaded on a sample holder, the motor begins to rotate as a result of a signal from the monitor, and drives the turntable clockwise until the next sample

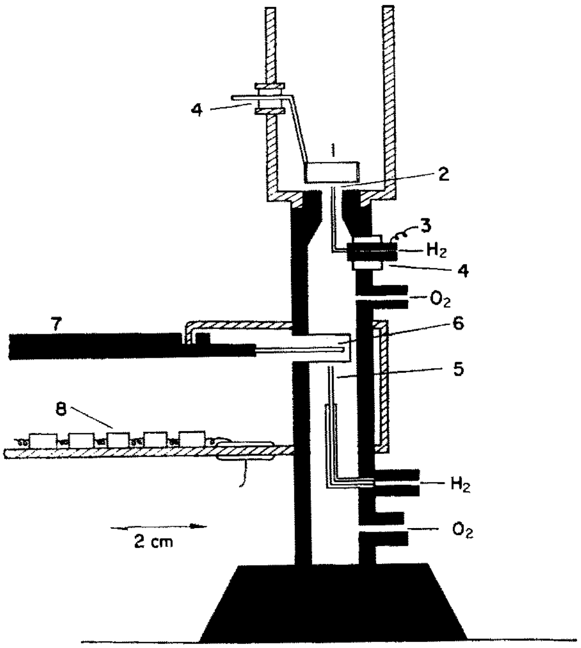


FIG. 3.—Hydrogen flame-ionization detector. ① Collector electrode (14 mm diameter, 6 mm high, Au); ② ionizing jet (anode, 0·6 mm bore, Pt); ③ terminal for applying potential to ionizing jet; ④ insulator; ⑤ evaporating jet (1 mm bore, Pt); ⑥ sample holder; ⑦ turntable; ⑧ heater for evaporating eluate.

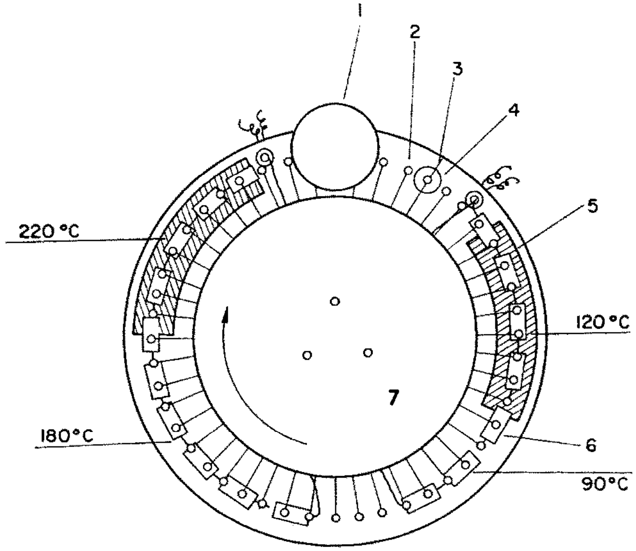


FIG. 4.—Heater assembly. ① Detector; ② sample holder; ③ shock absorber; ④ drain; ⑤ plate heater; ⑥ coil heater; ⑦ turntable.

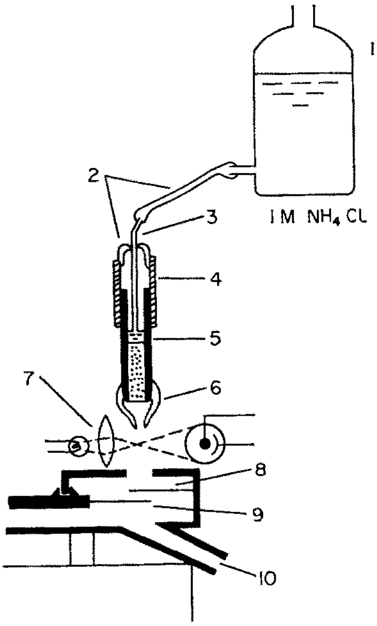


Fig. 5.—Chromatographic column and sampling device. ① Polyethylene bottle; ② polyethylene tube; ③ Pt tube (0·6 mm bore); ④ vinyl chloride tube; ⑤ ion-exchange column (silica tube 4 mm bore); ⑥ polyethylene; ⑦ device for monitoring a drop of eluate; ⑧ shock absorber; ⑨ sample holder; ⑩ drain.

holder is positioned just below the column. Simultaneously a drop of effluent on another holder moves into the heater chamber. In the heating zone, the eluate is evaporated, leaving a solid metal salt on the sample holder. When the metal salt is inserted into the evaporating flame, a response from the collector electrode is obtained and recorded. Thus the elution chromatogram is obtained.

Reagents

Salts of alkali and alkaline earth metals used were analytical grade reagents and ammonium chloride was prepared from hydrogen chloride and ammonia. They were dissolved in demineralized water and their solutions were kept in polyethylene bottles. Hydrochloric acid was prepared by dissolving hydrogen chloride in demineralized water.

RESULTS

Characteristics of the ionization detector were investigated in detail. The detector showed a good response to microamounts of the metals, as shown in Table I.

TABLE I.—LIMIT OF DETERMINATION AND LINEAR DYNAMIC RANGE

Sample	Limit of determination (*mole*)	Linear dynamic range	Remarks
LiCl	5×10^{-12}	1:100	Mixing HCl
NaCl	4×10^{-13}	1:50	Mixing HCl
KCl	5×10^{-14}	1:100	
RbCl	3×10^{-14}	1:100	
CsCl	3×10^{-14}	1:100	
$CaCl_2$	3×10^{-12}	1:100	
$SrCl_2$	3×10^{-13}	1:50	
$BaCl_2$	3×10^{-13}	1:70	

Evaporating flame temp. 1430°C; ionizing flame temp. 1380°C.

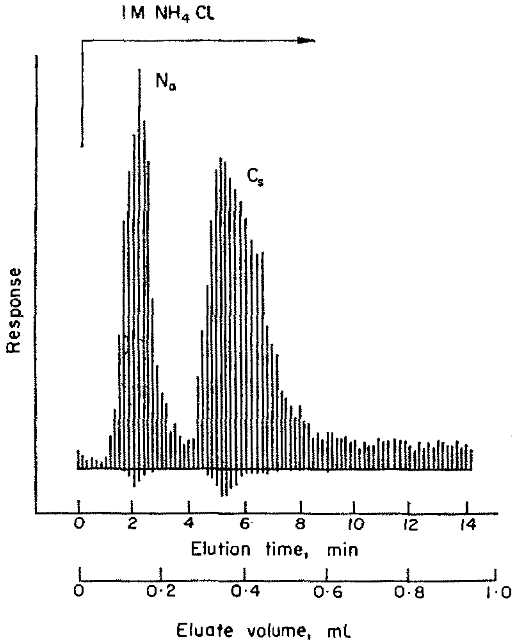


FIG. 6.—Ion-exchange chromatogram of sodium and caesium ions. Column, zirconium phosphate (20 mm × 13 mm^2); pretreatment with 2*M* HCl; eluent, 1*M* NH_4Cl; flow-rate, 0·072 ml/min. Sample: NaCl 2×10^{-9} mole, CsCl $2{\cdot}1 \times 10^{-10}$ mole.

An elution chromatogram (Fig. 6) of sodium and caesium ions was obtained with the chromatograph, with 1*M* ammonium chloride as eluent. Sodium and caesium could be determined from either the peak heights or the peak areas. The response did not return to zero after elution. It was considered that these baseline shifts occurred because of contamination with trace amounts of sodium or potassium in the preparation of the eluent. Therefore, the ammonium chloride, hydrochloric acid and demineralized water used should be highly purified.

Department of Industrial Analytical Chemistry
Faculty of Technology
Tokyo Metropolitan University
Setagaya-ku, Tokyo

SHUN ARAKI
SHIGETAKA SUZUKI
MASAAKI YAMADA

Summary—A new automatic chromatograph for ultramicro determination of alkali and alkaline earth metals has been developed. It combines a high-sensitivity hydrogen flame-ionization detector with ion-exchange chromatography. Zirconium phosphate was chosen as ion-exchanger.

Zusammenfassung—Ein neuer automatischer Chromatograph zur Ultramikrobestimmung von Alkalien und Erdalkalimetallen wurde entwickelt. Er vereinigt einen hochempfindlichen Wasserstoff-Flammenionisationsdetektor mit der Ionenaustauschchromatographie. Als Ionenaustauscher wurde Zirkoniumphosphat gewählt.

Résumé—On a élaboré un nouveau chromatographe automatique pour l'ultra-micro dosage de métaux alcalins et alcalino-terreux. Il combine un détecteur à ionisation de flamme d'hydrogène de haute

sensibilité avec la chromatographie d'échange d'ions. On a choisi le phosphate de zirconium comme échangeur d'ions.

REFERENCES

1. S. Araki, S. Suzuki and T. Hobo, *Bunseki Kagaku*, 1966, **15**, 27.
2. S. Araki, S. Suzuki, T. Hobo, T. Yoshida, K. Yoshizaki and M. Yamada, *ibid.*, 1968, **17**, 847.
3. S. Araki, S. Suzuki, T. Hobo and M. Yamada, *ibid.*, 1970, **19**, 493.

Talanta, 1972, Vol. 19, pp. 582 to 587. Pergamon Press Printed in Northern Ireland

Spectrophotometric studies on 5,7-dibromo-8-aminoquinoline chelates of some bivalent transition metals

(*Received* 19 *June* 1971. *Accepted* 21 *October* 1971)

WE HAVE BEEN studying 8-aminoquinoline and its derivatives in contrast with 8-quinolinol and as an example of an *N*,*N*-co-ordinately bonding organic reagent,[1-3] and now report on the 5,7-dibromo derivative.

EXPERIMENTAL

Reagents

Synthesis of 5,7-dibromo-8-aminoquinoline. Though 5,7-dibromo-8-aminoquinoline was obtainable by the reduction[4] of 5,7-dibromo-8-nitroquinoline, we synthesized it *via* the acetylation of 8-aminoquinoline.[5]

Commercial 8-aminoquinoline (2 g) was dissolved in glacial acetic acid (8–10 g) and placed in a 500-ml Erlenmeyer flask. In like manner, 4·47 g of bromine were separately dissolved in glacial acetic acid (18–23 g) by weight and stored in a separating funnel. The 8-aminoquinoline solution was vigorously agitated while being ice-cooled, and the bromine solution was added from the separating funnel dropwise. A fine yellowish-orange precipitate of 5,7-dibromo-8-acetylquinoline was obtained. Care was taken to cause it to agglomerate as little as possible. The precipitate was filtered off and dissolved in 50–100 ml of concentrated hydrochloric acid. The solution was poured into sufficient cooled water to yield a yellowish precipitate. This precipitate was recrystallized from methanol. The m.p. was 120–121°, and the yield 30%. Elemental analysis was as follows. Found: C 36·4%, H 2·1%, N 9·5%, Br 52·7%; calcd. for $C_9H_6N_2Br_2$: C 35·79%, H 1·99%, N 9·28%, Br 52·94%.

Metal ion solutions and solvents, *etc.*, to be used in the experiments were the same as previously reported.[2]

Dissociation constant of 5,7-dibromo-8-aminoquinoline (DBA)

The absorption spectra of $2{\cdot}02 \times 10^{-4}M$ DBA in 50% v/v aqueous dioxan were taken at various acidities (Fig. 1). At pH $>$ 1·9, the shape of the absorption spectrum was constant, with absorption maximum at 356 nm. At acidities of 0·05–1·0*N* (perchloric acid), the absorption spectra varied, with an isosbestic point at about 400 nm, and finally a new absorption maximum at 438 nm. The low-acidity spectrum is considered to be that of the neutral reagent and the high-acidity spectrum that of protonated reagent. Since it was thought that both chemical species were co-existent up to at least 0·50*N* acidity, the dissociation constant could be calculated.

For comparison, the absorption spectra of 8-aminoquinoline and 5,7-dibromo-8-aminoquinoline are shown in Fig. 2. The absorption spectrum of the reagent is shifted to longer wavelengths by the introduction of bromine atoms.

If HL^+ is the protonated form of the neutral reagent, L, the acid dissociation constant, K_a, is

$$K_a = \frac{[H^+][L]}{[HL^+]}\,. \tag{1}$$

If the absorbance at the determined wavelength of the solution is A, ε_{HL} and ε_L are the molar absorptivities of HL^+ and L respectively, C is the total concentration of L (*i.e.*, $C_L = [HL^+] + [L]$) and $A_0 = C_L\varepsilon_L$,

$$\frac{C_L}{(A - A_0)} = \frac{1}{(\varepsilon_{HL} - \varepsilon_L)} + \frac{K_a}{[H^+](\varepsilon_{HL} - \varepsilon_L)} \tag{2}$$

sensibilité avec la chromatographie d'échange d'ions. On a choisi le phosphate de zirconium comme échangeur d'ions.

REFERENCES

1. S. Araki, S. Suzuki and T. Hobo, *Bunseki Kagaku*, 1966, **15**, 27.
2. S. Araki, S. Suzuki, T. Hobo, T. Yoshida, K. Yoshizaki and M. Yamada, *ibid.*, 1968, **17**, 847.
3. S. Araki, S. Suzuki, T. Hobo and M. Yamada, *ibid.*, 1970, **19**, 493.

Talanta, 1972, Vol. 19, pp. 582 to 587. Pergamon Press Printed in Northern Ireland

Spectrophotometric studies on 5,7-dibromo-8-aminoquinoline chelates of some bivalent transition metals

(*Received* 19 *June* 1971. *Accepted* 21 *October* 1971)

We have been studying 8-aminoquinoline and its derivatives in contrast with 8-quinolinol and as an example of an *N,N*-co-ordinately bonding organic reagent,[1-3] and now report on the 5,7-dibromo derivative.

EXPERIMENTAL

Reagents

Synthesis of 5,7-dibromo-8-aminoquinoline. Though 5,7-dibromo-8-aminoquinoline was obtainable by the reduction[4] of 5,7-dibromo-8-nitroquinoline, we synthesized it *via* the acetylation of 8-aminoquinoline.[5]

Commercial 8-aminoquinoline (2 g) was dissolved in glacial acetic acid (8–10 g) and placed in a 500-ml Erlenmeyer flask. In like manner, 4·47 g of bromine were separately dissolved in glacial acetic acid (18–23 g) by weight and stored in a separating funnel. The 8-aminoquinoline solution was vigorously agitated while being ice-cooled, and the bromine solution was added from the separating funnel dropwise. A fine yellowish-orange precipitate of 5,7-dibromo-8-acetylquinoline was obtained. Care was taken to cause it to agglomerate as little as possible. The precipitate was filtered off and dissolved in 50–100 ml of concentrated hydrochloric acid. The solution was poured into sufficient cooled water to yield a yellowish precipitate. This precipitate was recrystallized from methanol. The m.p. was 120–121°, and the yield 30%. Elemental analysis was as follows. Found: C 36·4%, H 2·1%, N 9·5%, Br 52·7%; calcd. for $C_9H_6N_2Br_2$: C 35·79%, H 1·99%, N 9·28%, Br 52·94%.

Metal ion solutions and solvents, *etc.*, to be used in the experiments were the same as previously reported.[3]

Dissociation constant of 5,7-dibromo-8-aminoquinoline (DBA)

The absorption spectra of $2{\cdot}02 \times 10^{-4}M$ DBA in 50% v/v aqueous dioxan were taken at various acidities (Fig. 1). At pH $>$ 1·9, the shape of the absorption spectrum was constant, with absorption maximum at 356 nm. At acidities of 0·05–1·0*N* (perchloric acid), the absorption spectra varied, with an isosbestic point at about 400 nm, and finally a new absorption maximum at 438 nm. The low-acidity spectrum is considered to be that of the neutral reagent and the high-acidity spectrum that of protonated reagent. Since it was thought that both chemical species were co-existent up to at least 0·50*N* acidity, the dissociation constant could be calculated.

For comparison, the absorption spectra of 8-aminoquinoline and 5,7-dibromo-8-aminoquinoline are shown in Fig. 2. The absorption spectrum of the reagent is shifted to longer wavelengths by the introduction of bromine atoms.

If HL^+ is the protonated form of the neutral reagent, L, the acid dissociation constant, K_a, is

$$K_a = \frac{[H^+][L]}{[HL^+]}\,. \tag{1}$$

If the absorbance at the determined wavelength of the solution is A, ε_{HL} and ε_L are the molar absorptivities of HL^+ and L respectively, C is the total concentration of L (*i.e.*, $C_L = [HL^+] + [L]$) and $A_0 = C_L\varepsilon_L$,

$$\frac{C_L}{(A - A_0)} = \frac{1}{(\varepsilon_{HL} - \varepsilon_L)} + \frac{K_a}{[H^+](\varepsilon_{HL} - \varepsilon_L)} \tag{2}$$

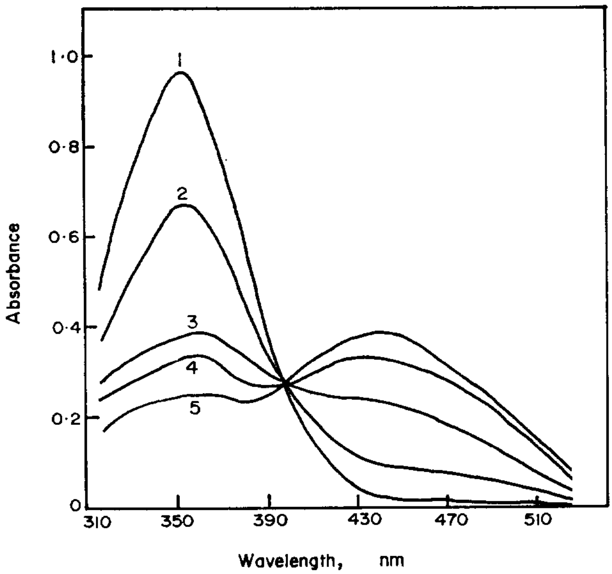


FIG. 1.—Absorption spectra of 2·02 × $10^{-4}M$ 5,7-dibromo-8-aminoquinoline. *1*—pH 1·85; *2*—0·10*M* $HClO_4$; *3*—0·25*M* $HClO_4$; *4*—0·50*M* $HClO_4$; *5*—1·00*M* $HClO_4$.

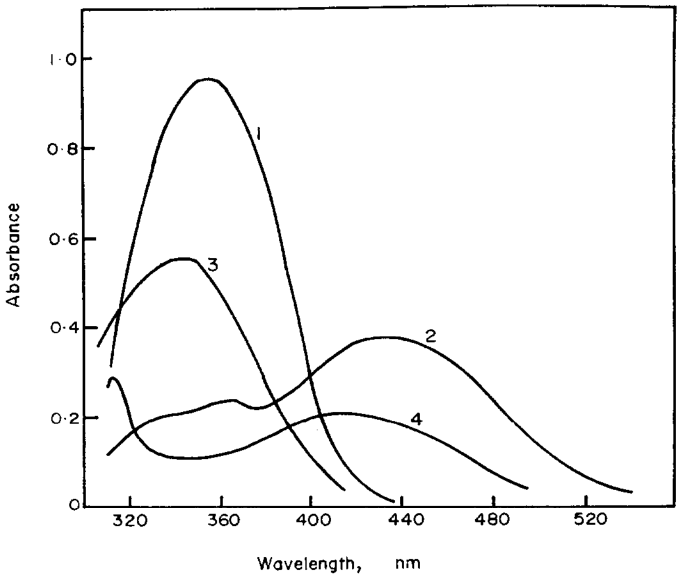


FIG. 2—Absorption spectra of 8-aminoquinoline and 5,7-dibromo-8-aminoquinoline. *1*—5,7-Dibromo-8-aminoquinoline; *2*—5,7-Dibromo-8-aminoquinoline (protonated form); *3*—8-Aminoquinoline; *4*—8-Aminoquinoline (protonated form). Concentrations 2·02 × $10^{-4}M$.

If the concentration of the reagent is kept at $2{\cdot}02 \times 10^{-4}M$, and the concentration of perchloric acid is varied from 0·10 to 0·25M, a linear relationship is found between $C_a/(A - A_0)$ and $1/[H^+]$. From these results, the acid dissociation constant of 5,7-dibromo-8-aminoquinoline can be found by the method of least squares. An average value, K_a, $7{\cdot}54 \times 10^{-2}$ (pK_a 1·1) was obtained, the individual values being 7·73, 7·72 and 7·18 (all $\times 10^{-2}$) from measurements at 430, 460 and 470 nm respectively.

This is large compared with that of the constant of 8-aminoquinoline ($1{\cdot}58 \times 10^{-4}$) because the electron-attracting power of the bromine atoms in the 5th and 7th positions reduces the electron density on the ring nitrogen atoms.

Absorption spectra of 5,7-dibromo-8-aminoquinoline chelate of copper

With $2{\cdot}02 \times 10^{-4}M$ DBA in 50% v/v dioxan–water at an acidity of 1·0M perchloric acid, variation of the copper(II) concentration from $2{\cdot}19 \times 10^{-4}$ to $2{\cdot}19 \times 10^{-2}M$ gave variation of the absorption spectra, relative to a solvent blank (Fig. 3). The absorption maximum was at 316 nm and the isosbestic point at 348 nm. It is considered that when copper is in excess only one type of chelate is formed in 1·0M perchloric acid.

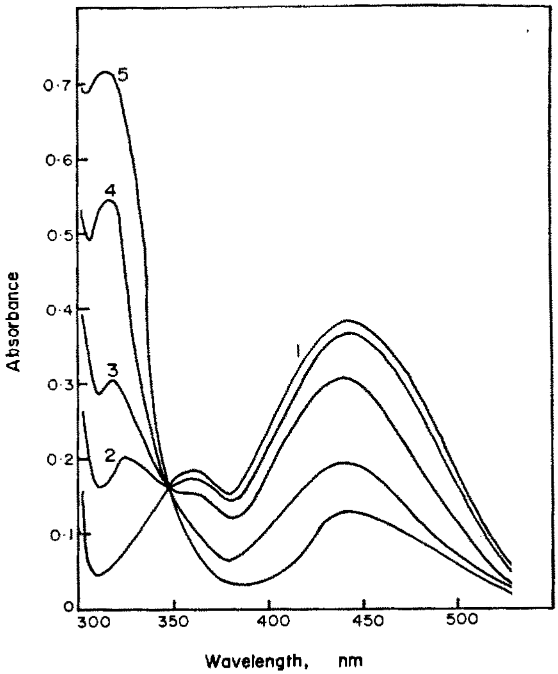


FIG. 3.—Absorption spectra of copper chelate of 5,7-dibromo-8-aminoquinoline. Reagent $2{\cdot}02 \times 10^{-4}M$, *1*—Reagent only; *2*—[Cu] $1{\cdot}09 \times 10^{-3}M$; 3—[Cu] $3{\cdot}29 \times 10^{-3}M$; *4*—[Cu] $1{\cdot}09 \times 10^{-2}M$; *5*—[Cu] $2{\cdot}19 \times 10^{-2}M$.

Composition and stability constant of 5,7-dibromo-8-aminoquinoline chelate of copper

If the reagent reacts with copper according to

$$Cu^{2+} + nHL^+ \rightleftharpoons CuL_n^{2+} + nH^+ \tag{3}$$

then

$$K_1 = \frac{[CuL_n^{2+}][H^+]^n}{[Cu^{2+}][HL^+]^n} \tag{4}$$

If the initial concentrations of copper and reagent are C_{Cu} and C_L and the concentration of the chelate is x (all in mole/l.),

$$K_1 = \frac{x[H^+]^n}{(C_{Cu} - x)(C_L - nx)^n} \tag{5}$$

Under these conditions, as the isosbestic point in Fig. 3 and the molar ratio method show, the composition of the chelate is 1:1. Thus when L as well as HL^+ is taken into account

$$K_1 = \frac{x\{[H^+] + K_a\}}{C_{Cu}/(C_L - x)} \tag{5a}$$

If ε_{CuL}, ε_L and ε_{HL} are the molar absorptivities of the chelate, L and HL^+, the total absorbance is A and the absorbances of L and HL^+ are A_L and A_{HL^+} respectively, it follows that

$$A = \varepsilon_{CuL}x + \varepsilon_{HL}\left\{\frac{[H^+](C_L - x)}{[H^+] + K_a}\right\} + \varepsilon_L\left\{\frac{K_a(C_L - x)}{[H^+] + K_a}\right\} \tag{6}$$

and

$$\frac{C_L}{\left(A - \frac{A_{HL}[H^+]}{[H^+] + K_a} - \frac{A_L K_a}{[H^+] + K_a}\right)} = \frac{[H^+] + K_a}{C_{Cu}K_1\left(\varepsilon_{CuL} - \frac{\varepsilon_{HL}[H^+]}{[H^+] + K_a} - \frac{\varepsilon_L K_a}{[H^+] + K_a}\right)} + \frac{1}{\left(\varepsilon_{CuL} - \frac{\varepsilon_{HL}[H^+]}{[H^+] + K_a} - \frac{\varepsilon_L K_a}{[H^+] + K_a}\right)} \tag{7}$$

If the concentration of the reagent is $2{\cdot}02 \times 10^{-4}M$ and the concentration of copper(II) ion varies from $7{\cdot}07 \times 10^{-3}$ to $1{\cdot}52 \times 10^{-2}M$, the acidity is maintained at $0{\cdot}45N$ with perchloric acid and the relationship between the left-hand side and $1/C_{Cu}$ in formula (7) is plotted, a linear relationship is obtained. Values of the equilibrium constant for the system were obtained by applying the methods of least squares to this curve. They were 14, 16 and 18 (mean 16) for measurements at 320, 325 and 330 nm. Log $k_1 = 2{\cdot}3$ was obtained as the stability constant of the 1:1 complex when K_a was taken as $7{\cdot}54 \times 10^{-2}$, and an ionic strength of 0·50 and a temperature of 25·0 ± 0·1° were maintained.

Absorption spectra and stability constant of 5,7-dibromo-8-aminoquinoline chelates of other metals

The method was also applied to the determination of the equilibrium constants for the 1:1 chelates formed with nickel, zinc, cobalt and cadmium (Table I). The stability constants are in Table II.

CONCLUSION

The results are summarized in Table II, which also includes those for 8-aminoquinoline and 8-quinolinol. It is seen that the electron-withdrawing effect of the bromine atoms leads to relatively

TABLE I.—EQUILIBRIUM CONSTANTS OF 5,7-DIBROMO-8-AMINOQUINOLINE CHELATES.

Wavelength, *nm*	*K*			
	Ni	Zn	Co	Cd
310	—	5·4	—	—
315	—	3·1	17	—
320	4·3	4·1	—	—
325	4·9	—	13	2·7
330	4·2	—	9	2·7
335	—	—	—	2·9
Mean value	4·5	4·2	13	2·8

TABLE II.—ACIDITY (pK_a) AND STABILITY CONSTANTS (LOG k) IN 50% V/V AQUEOUS DIOXAN.

Reagent	pK_a	log k					
		Cu	Ni	Zn	Co	Cd	Pb
8-Aminoquinoline*	3·80	5·5	4·1	3·7	—	1·9	—
5,7-Dibromo-8-aminoquinoline	1·12	2·3	1·8	1·8	2·2	1·6	—
8-Quinolinol	5·02†	13·49‡	11·44‡	9·96‡	10·55‡	9·43‡	10·61‡

* Reference 2.

† Reference 6.

‡ Reference 7.

low stability constants. The absorption curve of the chelate is shifted to longer wavelengths and greater molar absorptivities. The stability constants almost follow the Irving-Williams order, but that of the cobalt(II) chelate is greater than expected.

5,7-Dibromo-8-aminoquinoline is not thought to be particularly superior to 8-quinolinol as an analytical reagent, but it seems to provide information on the influence that different atoms exert on the formation of chelates.

Department of Chemistry
Faculty of Science
Ibaraki University
Mito, Japan

KATSUMI YAMAMOTO
HIROSHI TABATA

Summary—The acid dissociation constant of 5,7-dibromo-8-aminoquinoline and the stability constant of 1:1 chelates of some bivalent transition metals were determined spectrophotometrically in 50% v/v dioxan-water medium at an ionic strength of 0·50 at 25·0 ± 0·1° and compared with those of 8-aminoquinoline. The dissociation constant was found to be $7{\cdot}54 \times 10^{-2}$ and the stability constants (log K_1) were 2·3 (copper), 1·8 (nickel), 1·8 (zinc), 2·2 (cobalt) and 1·6 (cadmium), respectively. The dissociation constants are greater and the stability constants smaller than the corresponding values for 8-aminoquinoline and 8-quinolinol.

Zusammenfassung—Die Säuredissoziationskonstante von 5,7-Dibrom-8-aminochinolin und die Stabilitätskonstanten von 1:1-Chelaten einiger zweiwertiger Übergangsmetalle wurden spektrophotometrisch in 50 Vol.-% Dioxan-Wasser bei einer Ionenstärke von 0,50 bei 25,0 ± 0,1° gemessen und mit denen von 8-Aminochinolin verglichen. Die Dissoziationskonstante beträgt $7{,}54 \cdot 10^{-2}$ und die Stabilitätskonstanten (log K_1) 2,3 (Kupfer), 1,8 (Nickel), 1,8 (Zink), 2,2 (Kobalt) und 1,6 (Cadmium). Die Dissoziationskonstante ist größer und die Stabilitätskonstanten kleiner als die entsprechenden Werte bei 8-Aminochinolin und 8-Hydroxychinolin.

Résumé—On a déterminé spectrophotométriquement la constante de dissociation acide de la 5,7-dibromo 8-aminoquinoléine et les constantes de stabilité de chélates 1:1 de quelques métaux de transition bivalents dans le milieu dioxane-eau 50% v/v, à une force ionique de 0,50 à 25,0 ± 0,1°, et on les a comparées à celles de la 8-aminoquinoléine. On a trouvé que la constante de dissociation est de $7{,}54 \times 10^{-2}$ et les constantes de stabilité (log K_1) sont 2,3 (cuivre), 1,8 (nickel), 1,8 (zinc), 2,2 (cobalt) et 1,6 (cadmium) respectivement. Les constantes de dissociation sont plus grandes et les constantes de stabilité plus petites que les valeurs correspondantes pour la 8-aminoquinoléine et la 8-hydroxyquinoléine.

REFERENCES

1. K. Yamamoto, K. Ametani and K. Amagai, *Bunseki Kagaku*, 1967, **16**, 229.
2. K. Yamamoto and K. Ohashi, *Nippon Kagaku Zasshi*, 1969, **90**, 1138.
3. K. Yamamoto and Y. Noda, *Bunseki Kagaku*, 1970, **19**, 112.
4. A. Claus and A. Ammelburg, *J. Prakt. Chem.*, 1894, **50**, 34.
5 A. Claus and E. Setzer, *J. Prakt. Chem.*, 1896, **53**, 401.
6. R. Näsänen, P. Lumme and A. L. Mukula, *Acta Chem. Scand.*, 1951, **5**, 1199.
7. W. D. Johnston and H. Freiser, *J. Am. Chem. Soc.*, 1952, **74**, 5239.

Talanta, 1972, Vol. 19, pp. 589 to 621. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW†

ANALYTICAL MASS SPECTROMETRY

J. R. MAJER
Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.

(*Received* 12 *July* 1971. *Accepted* 11 *November* 1971)

Summary—A review is made of the basic theory, instrumentation and application of mass spectrometry, with special reference to the development of the equipment and its impact on the scope of application.

THE IONIZATION PROCESS

ANALYSIS by mass spectrometry depends upon the segregation of ionized molecules in magnetic, electric or radiofrequency fields. The ionization process which precedes this separation must take place in the gas phase and this imposes certain limitations on the technique, which are discussed later. Mass spectrometry is best introduced by using its relationship to other physical techniques based upon ionization. The ionization process may be described most generally by the interaction of a species M, which may be a molecule, an atom or a free radical, with a second species X, which may be an electron, a photon, an ion, a fast molecule or even a high potential gradient. M may be considered to be in thermal equilibrium with its surroundings but X must have a certain minimal energy content (E) which is greater than the binding energy of the electron in the lowest energy orbital in M, *i.e.*, the lowest ionization potential (I) of M. As a result of this interaction the lowest-energy electron is ejected and an ion M^+ is formed. For cases in which E is greater than I the excess of energy will be partitioned between the ion (E_1) and the electron (E_2). As the free electron is so light when compared with even a small polyatomic ion, any translational energy released in the process will be almost completely retained by the electron, which can of course retain no other form of energy. The ion M^+ on the other hand, although it has no translational energy, may have excitation energy (E_1) which may be electronic, vibrational or rotational.

$$\begin{array}{ccccccc} M & + & X(E) & \rightarrow & \mathrm{M}^+(E_1) & + & e(E_2) \\ n_\mathrm{M} & & n_\mathrm{X} & & n_1 & & n_2 \end{array}$$

In order to examine the consequences of this interaction in a real environment we must assume an assembly of particles of species M, their number being n_M. The number of particles of species X, which will most normally be measured as a flux, is n_X and the numbers of ions and electrons produced will be n_1 and n_2 respectively. Except in the case of multiple ionization n_1 and n_2 will be equal.

There are obviously two ways of investigating the ionization process experimentally: either the number of ions or the number of electrons may be measured. Such measurements are most commonly made by collecting the charged species with electrode assemblies across which the appropriate potential gradients are applied.

---

† For reprints of this review, see Publisher's announcement near end of this issue.

It is most convenient to investigate ionization as a continuous process so that n_M is kept constant by maintaining a flux or current of X through the assembly of molecules, atoms or radicals M. The resulting numbers of ions and electrons may now also be measured as fluxes, *i.e.*, numbers of ions or electrons per second or, more familiarly, electric currents. Let us suppose that n_M and n_X are kept constant while E is varied. The electron current n_2/t (where t is time) is now measured, for example, by inserting a pair of polarized electrodes into the cell in which M and X are interacting. If the electron current n_2/t is plotted against the energy E, the result is a typical ionization curve with a very steep rise in n_2/t as E rises above the ionization potential of M. When X is a photon then E may be very sharply defined by the wavelength of X and the ionization potential may be measured with considerable precision. When X is an electron, E is not precisely defined, as it is not very easy to obtain a beam of monochromatic electrons of suitable intensity. As electrons are normally produced from a white hot tungsten or rhenium filament they retain a Boltzmann distribution of energy $\pm\Delta E$ which is an appreciable fraction of a volt. As a result the inflection in the ionization curve is less precisely defined and the value of the ionization potential less certain. Now let us consider an alternative experiment in which the energy E is kept constant and considerably greater than the ionization potential of M. Instead of the total ionization current n_2/t being measured, the energy distribution in the emitted electrons is determined. This may be achieved experimentally by interposing a retarding potential grid between the two collecting electrodes or more elaborately by passing a beam of the emitted electrons through a transverse electric field and dispersing them according to their velocity. A plot is now made of E_2' against n_2'/t where E_2' is the energy in any emitted electron and n_2' is the number of electrons having such a translational energy. Then $\sum n_2' = n_2$. The difference between the energy of the projectile (E) and the translational energy of the emitted electron (E_2') is equal to that energy retained by the ion M^+. When X is a photon of high energy, this curve may be recognized as the photoelectron spectrum. Such a curve will have several maxima corresponding to the ionization of electrons in orbitals of different energies. In addition, for simple molecules, the maxima may reveal structure due to the formation of the ion in a variety of excited states. This experiment gives information about the energies of orbitals in polyatomic molecules in addition to the lowest ionization potential. Similar information is theoretically available if X is not a photon but an electron. Once again however, there is the problem of the energy spread experienced with electron beams. Electron monochromators are now being developed, however, giving currents as high as 10^{-8} A with an energy spread of as little as 20 mV. Combinations of two of these devices have been used to provide determinations of the energy distribution of emitted electrons, and a new spectroscopic technique, electron energy loss spectroscopy, is being developed. Once again the information available with this technique is concerned with the energies of orbitals in simple polyatomic molecules rather than with structures.

The alternative method of investigating the ionization process is by measuring the ion current rather than the electron current. A plot of n_1/t against E once again provides a method of determining the ionization potential of M. The results are more precise when X is a photon rather than an electron but the measurement of ionization potentials from the ionization efficiency curves obtained with mass spectrometers is common practice and various extrapolation procedures and deconvolution devices are used to increase precision of the determination. When X is an ion, the situation is complicated by the involvement of the recombination energy of the projectile ion with an electron. This complication also arises with the other techniques mentioned above. A measurement of the ratio n_1/n_M gives a measure of the ionization cross-section of the molecule M. The ionization efficiency curve, which is a plot of n_1/t against E does not give any information about the higher ionization potentials of polyatomic molecules because it is not possible to identify the variation of cross-section with E for any specific ionization process in which an electron of particular energy is being removed, except in the simplest possible case of the hydrogen atom or possibly the hydrogen molecule. Energy analysis of the ion current reveals no information, because the translational energy is all removed by the electron and at present there is little or no possibility of the determination of the nature of the excited states of ions.

While however, little information of this type is available from an examination of the ion current, the technique of mass spectrometry is based on an alternative way of looking at the ion current. This arises because it is possible to segregate ions not according to their energy content but according to their relative mass. The various methods by which this segregation is achieved are discussed below and it is only necessary to point out that the assembly of the species M may now consist of a number of different molecules, atoms or radicals. Each of these will be converted into the appropriate ions M^+ and it is now possible to measure all the individual ion currents n_1/t and to plot n_1/t against the mass of the ion m. Such a plot constitutes a mass spectrum.

$$m \sum_{0}^{M} n_1' = n_1$$

If the assembly of species is, for example, a mixture of rare gases so that the only ionization processes possible were the production of the singly-charged rare gas ions then it is possible to analyse the mixture by mass spectrometry. Both n_M and n_X must be kept constant so that the rate of production of ions is constant. The individual ion currents of the species M are then proportional to the partial pressures of the species M in the mixture and the sum of all these currents is equal to the total ion current n_1/t. This situation is rather similar to the conditions of fluorescence analysis where the incident radiation is analogous to the electron beam and the fluorescent radiation is analogous to the ion beam, the wavelength and mass being characteristic of the species M. There are very few cases in which this very simple form of mass spectrometry has a modern application. There are two examples worth recording however, the first medical and the second cosmochemical. The most readily available gas mixture is the atmosphere and a mass spectrum of air readily reveals the separation of the ion currents due to oxygen, nitrogen, carbon dioxide and argon. The efficiency of a patient's respiration may be assessed by taking samples of the atmosphere from his lungs. This process can be carried out continuously and can show not only the state of the patient's breathing but also the concentration of any foreign gas introduced to induce anaesthesia.

The second application also deals with the analysis of atmospheres, but in extra-terrestrial situations. The development of very small light mass spectrometers, now referred to as "flyable" instruments, permits their transportation by rocketry to a number of remote situations. The molecule and ion concentrations in the outer layers of the earth's atmosphere may be examined by carrying a small mass spectrometer on a rocket and relaying the information which it gathers to a remote ground station by radio. An extension of this principle will allow the examination of a number of planetary atmospheres.

The dissociation of excited ion-molecules

The great value of mass spectrometry as an analytical technique does not derive from simple applications such as these, but from a quite distinct and separate result of the initial ionization process. For ionization to take place the energy in the electron must exceed the lowest ionization potential of the molecule. It must therefore have a value of E which is at least 15 eV since the ionization potentials of all molecules lie between 6 and 15 eV. It is common practice, in order to obtain sufficiently high values of the cross-section n_I/n_M which determines the sensitivity, to choose values of E in the 50–100 eV range. The cross-section n_I/n_M does not vary significantly above 100 eV but falls off rapidly below 50 eV. Although not all of the energy in the projectile electron is transferred to the molecule, the result of the ionization process may be the production of an ion with a considerable excess of energy (E_I). As the excited molecule ion is normally produced under high vacuum conditions (approximately 10^{-6} mm Hg) this excess of energy cannot be lost by collision with other molecules. It can thus only be reduced by the emission of a photon, a comparatively unlikely event, or by the molecule ion undergoing dissociation or rearrangement. As the bond dissociation energy of all chemical single bonds lies between 2 and 5 eV the transfer of a small fraction of the translational energy of the incident electron can result in the fission of a number of chemical bonds with the production of radicals and smaller ions. Because of the large excess of energy the dissociation process has two important features. The first is that there are a number of alternative modes of dissociation available and the diversity of these decompositions is further enhanced by the fact that the electrons have an energy spread $\pm\Delta(E)$ and may transfer a variable amount of their translational energy to the molecule, depending on the nearness of approach and the consequent intensity of interaction. As a result the excited molecule ion may dissociate in a number of parallel and consecutive reactions. If E is high, the molecule ion is most likely to react by breaking chemical bonds; if E is low the molecule ion is most likely to rearrange. The second feature is that the rate constants for the dissociation processes are very high and the reactions have negligible energies of activation. As a result the rates of reaction are almost totally unaffected by experimental parameters other than E. This means that the ratios of the ion currents for the molecule, fragment and rearrangement ions will have constant values over wide variations of n_M or n_X or the temperature of the ionization cell. The relative intensities of the ion currents, which are responsible for the peaks in a mass spectrum, constitute what has come to be known as the cracking pattern of the molecule. It is the cracking pattern which is therefore substantially invariant and constitutes a fingerprint of the molecule in the same way that the infrared absorption spectrum does. It is thus possible to match the cracking pattern observed with a chemical compound measured upon one instrument with that of the same compound measured on a machine with a completely different geometry. This match is not as complete as that obtained with infrared or NMR spectra, but the usefulness of this near identity has led to the collection both privately and by industrial and government organizations of large libraries of mass spectral cracking patterns. The best known collection of spectra has been made by the American Petroleum Institute Research Project 44. A second rapidly growing collection is being amassed by the Mass Spectrometry Data Centre situated at Aldermaston. The reduction of these cracking patterns to digital form permits a direct comparison by computer, and several schemes are in operation by which the mass spectrum of an unknown compound may be compared with a library of the spectra of known compounds, held upon a disc in a computer memory.

One of the most severe problems encountered in the matching of spectra is the necessity of matching the purity of the standard and unknown samples. The presence of a substantial impurity in either may cause a mismatch so severe that the identity is lost. The effect of the minor constituent in distorting the mass spectrum may be further magnified by a difference in the rate of evaporation of the two components. With volatile samples this effect may be minimized by evaporating all of the sample into a reservoir from which the vapour flows into the ion source. When solid samples are being introduced into the source by the insertion-probe technique this is not possible. The situation is at its worst when isomers are being studied. There are only very small differences in the mass spectra of structural isomers and it is only possible to match the spectra of unknown and standard if the purity and method of sample admission are kept the same. Fortunately, there are two ways of dealing with this problem. The first is to use the technique of differential evaporation as discussed in the section describing quantitative methods, and the second is to combine mass spectrometric identification with some other technique of physical separation such as chromatography. Chromatography in one form or other is to be preferred because in general the resolution obtainable with chromatographic methods rises with the lowering of sample size, and mass spectrometry is capable of dealing with very small sample sizes, in some cases well below the detection limit of the normal colorimetric or fluorometric methods.

Chromatographic separation

It is not difficult to separate small quantities (micrograms) of complex organic compounds by paper chromatography. The area containing the spot of the unknown is eluted with an organic solvent, the solution is concentrated by evaporation, and the concentrate admitted directly to the mass spectrometer. It is unfortunate that this process is surprisingly variable: sometimes the resulting mass spectrum can be matched very well with that of a standard, at other times the solvent may extract from the paper not only the sample material but also a great deal of contamination from the paper itself. The amount and nature of this contamination are dependent not only on the nature of the paper but also on its previous history, *i.e.*, which solvents it has already been exposed to during the chromatographic separation. Some improvements are observed when paper chromatography is replaced by thin-layer chromatography, on silica gel, cellulose *etc.* It has been possible, for example, to separate drugs from whole blood by a single separation upon cellulose and to identify the drug by removing a small area of the thin layer with a spatula and extracting with the appropriate eluent, filtering the slurry, evaporating the solvent and transferring the residue to the ion source in the manner described in the experimental section. Further, in the case of some compounds it has been possible to show that this process may be quantitative, so that submicrogram quantities of the components of complex mixtures may be separately identified and determined.[1]

When the sample components are sufficiently volatile they may be separated by gas chromatography. The very high efficiencies of separation obtainable with these methods, which greatly exceed those possible with fractionating columns, and their ability to deal with very small sample sizes, have encouraged experimenters to combine them with mass spectrometry. The separation of a pair of compounds by gas–liquid chromatography depends not only upon differences in the volatility of the two components but also upon differences in their interaction with the involatile liquid into which they are partitioned from the gas phase. As a result it is possible to take advantage not only of simple solution forces but of specific chemical interactions. It is thus possible, for example, to separate the *cis* and *trans* isomers of many simple hydrocarbons by using an involatile liquid containing a silver salt with which the unsaturated compounds form transient complexes. In a similar fashion the isomers of aromatic hydrocarbons may be separated by including in the involatile liquid some polynitro compound capable of forming molecular complexes with the aromatic. In each case some small difference in the stability of these complexes is exploited and quite small quantities of the involatile liquid are required. On the other hand, separations involving conventional solution forces may be made possible by having a very much larger quantity of the involatile liquid, maintained as a very thin film, and considerably multiplying the number of equilibrations of the sample mixture with the liquid. The limit to this is set only by purely experimental considerations of size and carrier gas inlet pressure. However, by an appropriate choice of column length and involatile liquid composition, it is possible to separate the components of complex mixtures of chemically very similar compounds. As an example, with the most efficient columns (either glass capillaries lined with squalane, or narrow packed columns with the same material dispersed upon small mesh size inert support) it is possible to separate deuterated hydrocarbons from their protonated counterparts. Dodecadeuterocyclohexane may be separated from normal cyclohexane with a relatively inefficient column of about 2000 theoretical plates, hexadeuterobenzene is separated from benzene, and trideuterotoluene from toluene[2] with packed or capillary columns with an efficiency of 10,000–15,000 plates, and with the highest efficiency columns of above 100,000 plates, monodeuterobenzene can be separated from benzene. The success of separations has in the past been limited by the inability of the gas chromatographic technique to provide an unequivocal means of identifying the separated species. The idea of specific retention volumes as a unique physical property which could be used for identification purposes has not been enthusiastically accepted by gas chromatographers. The determination of this constant, which is independent of temperature, gas flow-rate, involatile liquid concentration and sample size, required such precisely defined operating conditions that it was seldom used. A more successful compromise was the relative retention volume in which the retention volume of the unknown was expressed as a fraction of that of some similar known substance. Some variations in the experimental parameters were rendered less important but the uncertainties remained. Uncertainty could be removed by segregating the components of the mixture as they emerged from the chromatographic column, by adsorption on silica gel or alumina or by the passage of the effluent through a trap cooled in liquid air. A separate adsorbent tube or liquid-air trap was required for each component of the mixture requiring identification. The sample components recovered in this way were then identified by a second technique. Such a two-stage separation and identification does, however, involve difficulties, mainly resulting from the problem of manipulating small amounts of volatile material. This has resulted in the development of a direct coupling of the effluent from the gas chromatograph to the inlet system of the mass spectrometer, so that there is no handling process after the injection of the sample mixture into the inlet of the gas chromatograph. The manner in which this has been achieved is discussed in the section dealing with instrumentation and it is only necessary to point out that the problem of matching unknown and standard spectra is considerably simplified when the purity of the specimen is so assured. Further, although the retention volume is not normally determined with sufficient precision to make it a primary means of identification, it provides a useful additional piece of evidence to back up the mass spectra identification.

In all the foregoing it has been assumed that there exists a library spectrum of the unknown, and the only problem is that of matching. While this may be the case for some experimentalists, even in a routine analytical laboratory there will be times when the analyst will be faced with the identification of a completely new compound from its mass spectrum.

As outlined earlier, the mass spectrum presents a record of the unimolecular decomposition of an assembly of highly excited molecular ions. The chemistry of the decomposition is unique, and no great reward is obtained by comparisons with ground state chemistry or with radiolysis. And yet the only structural information available from a mass spectrum is that which can be gleaned from an understanding of the way in which the molecule ion breaks down. There are three distinct approaches to the problem of extracting this information. The analyst may attempt to understand this novel type of chemistry so that he may deduce the structure of the molecule ion from recognized decomposition processes. This approach is analogous to that by which many natural products were identified by classical organic chemical degradations, *e.g.*, pyrolysis or dehydrogenation. The second approach is to change the ionization process so that a different dissociation route is traversed. The third approach, which will commend itself most readily to the analytical chemist since he may make use of much of his armoury of chemical identification methods, is to modify the sample itself by means of a known chemical reaction and to infer the structure from a comparison of the mass spectrum before and after the chemical process. This method is analogous to the preparation of a derivative with a known physical property such as a melting point, absorption spectrum, R_f value or cryoscopic molecular weight. Our present understanding of the chemistry of the decomposition of ions has in fact been largely accumulated by studies involving the second and third approaches, and Beynon[3] in this country and McLafferty[4] in the United States have been particularly successful in expanding our understanding of the mechanisms involved. While it has been stressed that the chemistry of ion decomposition cannot be interpreted with the aid of an understanding of ground state mechanisms alone, there are certain features or underlying principles of chemical theory which must apply with equal force to these very fast reactions. It would be expected that the effect of neighbouring groups upon each other would be reflected in the rates of decomposition. An extreme example of this would be the so-called "*ortho* effect" where much stronger interactions would be expected between groups when they are adjacent to each other as substituents on a benzene ring than when they are more remote. Such an effect is observed and the spectra of isomers such as those of the nitrophenols or the hydroxybenzaldehydes are appreciably different (Fig. 1).

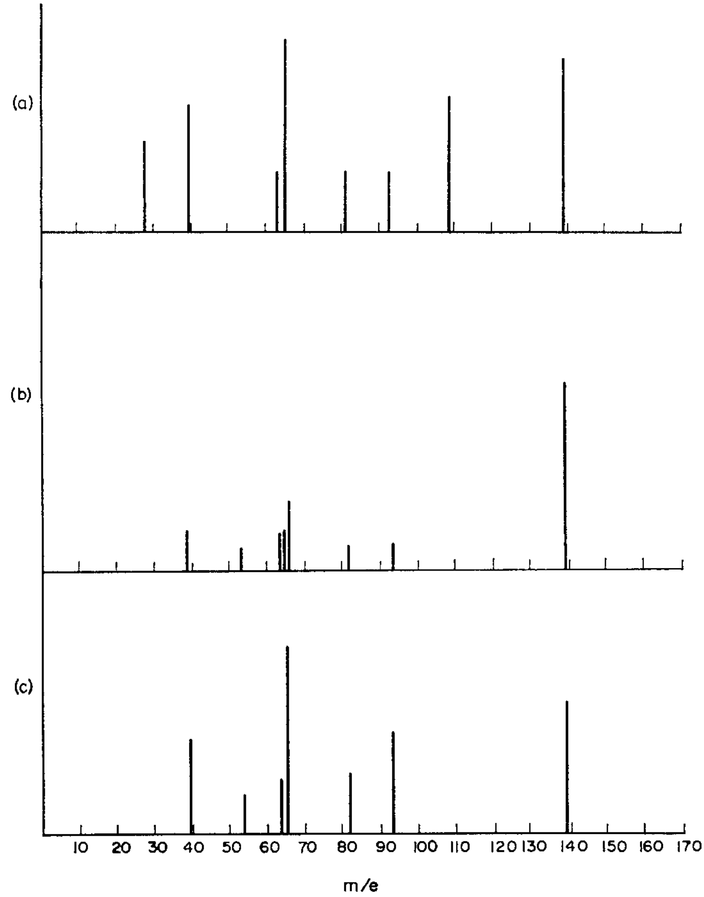


Fig. 1.—Mass spectra of nitrophenols: *a*, *p*-nitrophenol; *b*, *o*-nitrophenol; *c*, *m*-nitrophenol.

Since the energy is lost from the excited ion by breaking chemical bonds the strength of these bonds must have an effect upon the rate. As a result the rate of production of an ion from the molecule ion by the fission of a carbon–bromine bond would be expected to be much faster than if the same ion were being produced by the fission of a carbon–hydrogen bond, which has twice the bond dissociation energy. There are many examples in which this may be clearly demonstrated. The nature of the second species must also play a part in determining the rate of decomposition. Where the un-ionized fragment is a stable radical such as benzyl or allyl, then this dissociation is favoured. A very common example of the effect of the second species is when that species has a high electron affinity and so may readily form a negative ion with the release of up to 3 eV of energy. The most commonly observed example is the production of ion-pairs when compounds containing fluorine atoms are ionized. The high electron affinity of the fluorine atom results in the rapid dissociation of the molecule ion, and the mass spectra of most saturated fluorocarbons have negligibly small molecule ion peaks.[5] The most valuable information from a fundamental point of view would be the thermodynamic heats of formation of the ions, but although many values are available the thermochemical relationships have only been constructed for the simplest cases, and the main obstacle to their use in more complex systems is the lack of information about the excited states of the ions involved. If the mass spectrum represented only the results of the bond-breaking processes then the interpretation of most spectra would be greatly simplified. However, there are in addition a number of other processes occurring, leading to the formation of ions which could not arise by simple bond-breaking. The peaks in the mass spectra corresponding to ions produced in these processes were originally considered as noise, but recent improvements in instrumentation have provided more information about them and their recognition may actually aid structural analysis. These processes, which are normally called rearrangements, usually occur at low energies and result in the formation of an even-electron neutral species and an odd-electron ion, (*cf.* the bond-breaking process leads to the formation of an even-electron radical ion and an odd-electron atom or radical). An exception to this is when hydrogen atoms are involved. Hydrogen atoms appear to be quite mobile in the excited ion molecule and substantial rearrangements occur. Thus in the spectrum of 1,1,1-trideuterodimethyl sulphide[2] there are substantial peaks corresponding to the ions CD_2H^+ and CDH_2^+.[6] Another example of the mobility of atoms is the transfer to metal observed in the mass spectra of metal chelates. The spectrum of the titanium derivative of the diketone benzoyltrifluoroacetone exhibits peaks corresponding to ions in which one or two fluorine atoms have been transferred to the metal atom (Fig. 2). The elimination reactions referred to previously however may be more useful once they are understood. Certainly the most widely known of these rearrangement processes is the McLafferty rearrangement[7] in which the hydrogen atom gamma to a carbonyl or other electronegative group is transferred to the heteroatom with beta-cleavage of the molecular

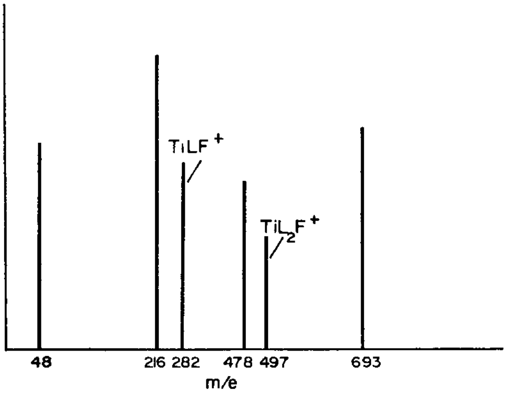


FIG. 2.—Mass spectrum of titanium benzoylacetonate, illustrating fluorine transfer to metal.

ion and the elimination of an unsaturated compound or a diradical (Fig. 3). Other examples include the elimination of CF_2 from atomatic compounds containing a CF_3 group, such as benzotrifluoride,[8] or the elimination of CO from aromatic ketones such as anthraquinone.[9]

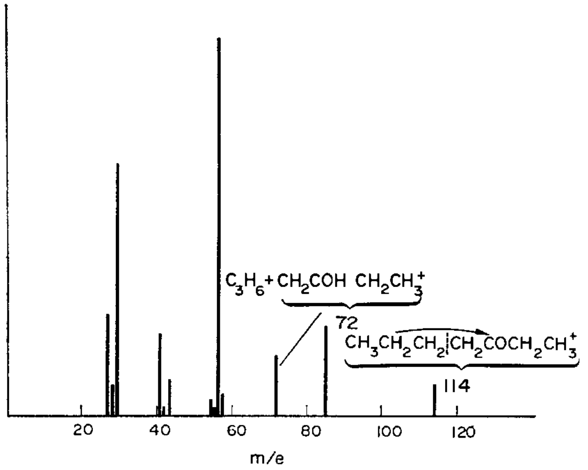


FIG. 3.—Mass spectrum of heptanone-3, illustrating the McLafferty rearrangement.

All these rearrangements lead to the formation of ions having an even mass (provided they do not contain an odd number of nitrogen atoms) and even-mass peaks other than molecule ion peaks are comparatively rare, so that it is easy to pick out the peaks due to rearrangement processes and to infer the structures from which they are formed.

In carrying out identification of unknown species by their mass spectrum alone, there are two techniques now available as a result of modern instrumentation, which are of the greatest assistance. The first of these is precise mass analysis which has been made possible by the development of high resolution instruments. The presently accepted mass scale uses carbon 12 as its standard, assigning it a mass of 12.000000. On this scale the mass of the hydrogen atom is 1.007825 while that of the oxygen atom is 15.994914. It follows that there is an appreciable difference in mass between ions having the same integral mass. Thus both carbon dioxide and propane ions have an integral mass of 44 but their precise masses of 43.989828 and 44.062600 differ by about 1 in 600. As a result a mass spectrometer with a resolution of 1000 can resolve the beams of carbon dioxide and propane ions when they are produced simultaneously and from the mass scale it is possible to say which is which. A higher resolution is required to resolve the mass doublet due to carbon monoxide and nitrogen molecule ions. It can be seen that an assembly of carbon, hydrogen and oxygen atoms gives a unique precise mass and this is true for any other atomic assembly. At the time of writing commerical mass spectrometers are available which have a mass resolution of 100,000 and masses of ions can be measured with a precision of 1 ppm. As a result it is possible to determine the atomic constitution of ions with a high degree of certainty. Taking, for example, the molecule ion of adrenaline, its precise mass is 183.089541 and the nearest precise mass to this which can be envisaged is 183.088195 which differs by one part in 180,000, which is considerably greater than the uncertainty of measurement. The atomic constitution is thus unequivocally determined as $C_9H_{13}O_3N$. The identification of the atomic composition from the precise mass can be carried out by the use of tables of the precise masses of atomic assemblies or may be done automatically with quite a simple computer programme. The atomic constitution of all ions represented in a mass spectrum can be identified provided that either the time or the instrumentation is available. It should be stressed, however, that despite the very great advance in understanding that such information provides, there is still at this stage no direct evidence as to the manner in which the atoms are linked together in the ions. It would be considered a reasonable assumption, on finding that peaks of mass 91 and 77 in the spectra of aromatic compounds were due to the atomic species $C_7H_7^+$ and $C_6H_5^+$, that these were in fact the benzyl and phenyl ions. There is evidence to the contrary, mainly arising from labelling studies, that these are seven membered ring and open-chain structures, respectively. Quantitative evidence about the structure of ions is scanty but there is good reason for believing that the doubly-charged ion of benzene no longer retains its cyclic structure.

The second technique which has been found useful in the study of ionic decomposition is that of metastable defocusing. It was pointed out in the earlier paragraphs that the reactions of ionic decomposition were extremely rapid and that the result of this was the consistency of the cracking pattern. In fact most of the chemistry is complete before the ion has left the source region of the instrument and proceeded to the analysis region, this journey taking a time of the order of a μsec. Some molecules in the ion source have relatively inefficient encounters with the ionizing electrons and as a result have lower amounts of excitation energy in the ions produced. The rate of dissociation of such ions is slower and weakly excited ions may escape from the source region of the instrument before undergoing reaction. The experimental result of this situation is that the ion, having acquired a velocity appropriate to its mass from the accelerating voltage gradient in the instrument, now changes its mass by the loss of a neutral fragment before being subjected to mass analysis. The magnetic field therefore brings this ion to a focus on the mass scale at a position which is neither the focus of the parent or the daughter ion but lower than either. In many cases the masses of the ions are related by the simple equation.

$$m^* = m_2^2/m_1$$

where m_1 is the parent mass, m_2 the daughter mass and m^* the apparent or metastable mass. The ions so produced have been erroneously named metastable ions and the peaks metastable peaks. These peaks may easily be identified in a mass spectrum by their appearance. They are most commonly very much wider than the normal peaks. This is due to the fact that the ionic decomposition is usually associated with the release of kinetic energy, which effectively increases the energy spread of the ion beam for that species only, and hence decreases the resolution, giving wider peaks. In fact there is a quantitative relationship between peak width and kinetic energy release and there have been a number of studies on this relationship, but of more general use is the facility of identifying the parent and daughter ion responsible for the metastable peak. Since the mass of each of these ions must be greater than that of the metastable peak position on the mass scale, and because there is normally a large ion current due to the parent ion, it is a fairly simple matter to find values of m_1 and m_2 which satisfy the equation. As an example, the mass spectra of most saturated hydrocarbons exhibit a peak at $m/e = 39{\cdot}1$ and the appropriate values of m_1 and m_2 for this metastable mass are 43 and 41 respectively. This means that the mode of decomposition can be identified, and on combining this technique with precise mass measurement it can be shown that the decomposition pathway is

$$C_3H_7^+ \rightarrow C_3H_5^+ + H_2$$

This of course does not imply that the $C_3H_7^+$ ion is either a propyl or an isopropyl ion; in fact, what evidence there is, arising from labelling studies, suggests a cyclic structure. In general, metastable peaks are less intense than those produced conventionally and the technique of metastable defocusing allows the operator to overcome this sensitivity problem and eliminate the difficulty of disentangling the normal and metastable spectra. The instrument is so adjusted that only those ions which have suffered a change in velocity as a result of a dissociation process taking place outside the ion source are able to pass a diaphragm situated after the energy selector of a double focusing instrument. The ion current due to ions formed within the ion source is not detected and the spectrum consists only of a series of metastable peaks, the intensity of which can be increased by increasing the amplification of the instrument, without at the same time increasing the signal due to the normal ion processes.[10] It is also possible to scan the spectrum in such a way as to identify all those decompositions associated with one particular ion.

The second approach in the identification of unknown compounds from their mass spectra is to gain additional information by varying the ionization process. The simplest way in which this may be achieved is to vary the energy in the ionizing electron beam. Many of the processes which are possible at energies of 70 eV cannot take place if the electron voltage is reduced to say 10 eV (see *e.g.*, Fig. 4). In some cases it may be possible to eliminate all the dissociation processes and obtain a spectrum which represents only the molecule ions of the sample components. This is however, easiest to achieve if the normal mass spectrum reveals a large molecule ion peak. Reducing the electron energy does not increase the total molecule ion current and may substantially reduce it, but it does increase the relative importance of the parent peak. An alternative to the reduction of electron energy is the substitution of the electron impact source by what has been called the field ionization source. If a molecule is exposed to a potential gradient which is similar to that existing at the outer electronic shells of the molecule then the outer low-energy electrons can escape and the molecule becomes ionized without the transfer of large amounts of excitation energy to the ion. A value of 10^8 V/cm is sufficient for this purpose and this can be created experimentally by a voltage of 10^5 V applied upon a sharp edge with a radius of a few hundred Å, such as a razor blade. The ions accelerated away from this edge are not highly excited and it is possible to create ions from molecules having weak chemical bonds, such as hydrates. Such species would not survive ionization by an electron impact source. Thus the spectrum produced by a field ionization source is very much simpler than that obtained with a conventional electron impact source and it is very much easier to identify the molecule ion.[11]

A further way in which ionization can take place has been studied by Field and relies upon ion–molecule interactions.[12] A conventional ion source is normally

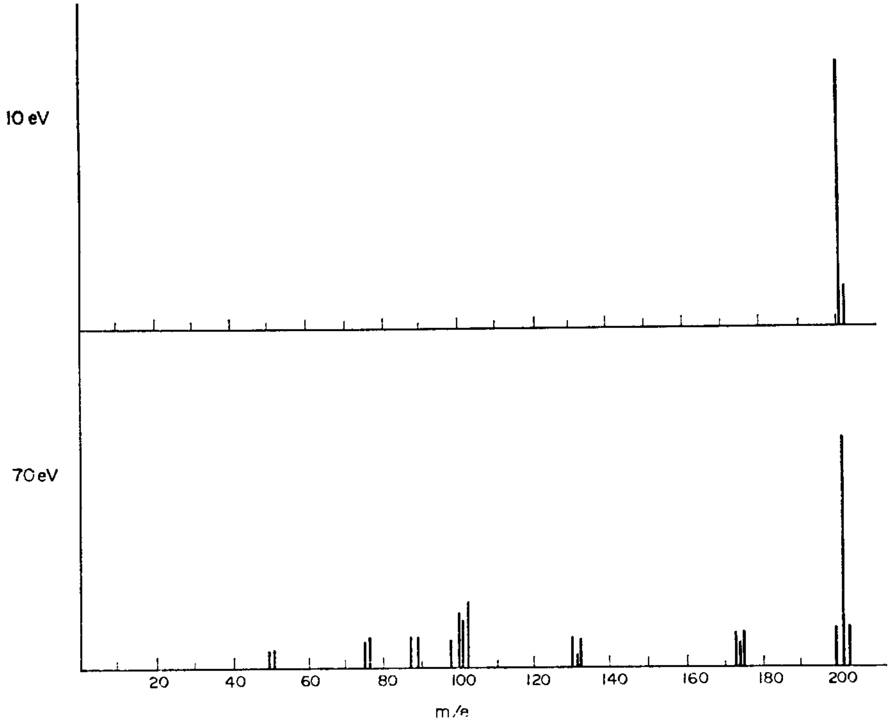


Fig. 4.—Mass spectrum of fluoranthene at 70 and 10 eV.

operated at a very low pressure so that the molecules have a long mean free path and secondary reactions are rendered insignificant. If, however, the pressure is allowed to rise above about 10^{-5} mm Hg the ion may interact with un-ionized gas molecules before it leaves the ion source. It has now become possible to eliminate the danger of producing gas discharges caused by the earthing of ion-accelerating voltages through a high pressure gas and to operate ion sources safely at pressures up to 1 mm Hg. If methane is ionized in such a source, then the methane ion, which is the initial result of the electron impact, abstracts a hydrogen atom from the methane gas to form CH_5^+.

$$CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3$$

If now a trace of a substance having a higher proton affinity is added to the methane, the proton is transferred to this molecule. The protonated molecule then decomposes in such a way that the charge remains with the fragment radicals. In this way an assembly of molecules gives rise to a mass spectrum with a different cracking pattern from that obtained by normal electron impact.

Finally, there is the purely chemical approach in which the sample substance is subjected to known reactions, the results of which are assessed by running additional mass spectra. The reactions chosen should be those which occur at room temperature (if possible) and lead to the formation of a derivative having a higher molecular weight than the original sample substance. There are a number of such reactions described in the literature, for the quantitative analysis of small amounts of compounds containing functional groups. The simplest possible reaction is that of deuteration. The sample is merely mixed with heavy water and allowed to equilibrate. Any labile hydrogen atoms such as those attached to oxygen atoms in hydroxyl or carboxyl groups will be replaced by deuterium. The result is that the mass spectrum, while retaining its overall pattern, will move to higher *m/e* values for those peaks which correspond to ions which have suffered deuteration. It is thus an easy matter to determine the number of hydrogen atoms replaced and which therefore were attached to oxygen. A second specific reaction which may be used with advantage is the conversion of aldehydes into aldoximes with hydroxylamine hydrochloride solution. For each aldehyde group converted the spectrum moves 15 mass units. The simplicity of this approach is that these reactions may be carried out on the microgram scale on the probe of the mass spectrometer, and the reaction products analysed without any pretreatment. As an example, the following three spectra (Fig. 5) show the spectrum of an alkaloid precursor[13] and its reaction products with heavy water and hydroxylamine hydrochloride. The presence of one hydroxyl and one aldehyde group is clearly indicated and the structure of the compound has been shown to be

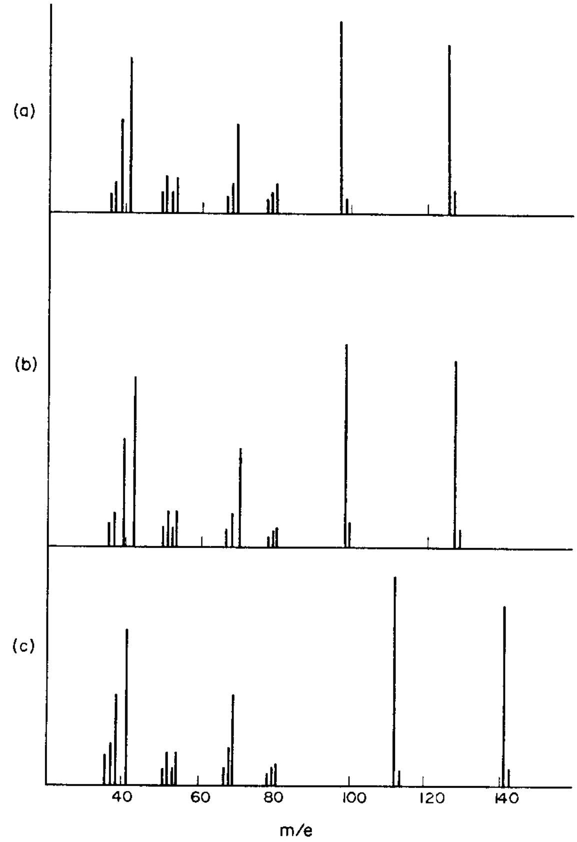
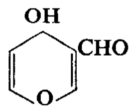


FIG. 5.—Determination of structure by the formation of derivatives: *a*, hydroxypyrone aldehyde; *b*, after deuteration; *c*, after forming the oxime.



INSTRUMENTATION

Mass spectrometry shares with the technique of molecular beams the distinction of being the physical method slowest to receive widespread acceptance and exploitation by the chemist. Both were being used by the physicist before the last war and it is only recently that the mass spectrometer has taken its place beside optical spectrometers in the laboratory for routine sampling and analysis. In no other technique has there been such widespread proliferation of instrumentation or so wide an application to diverse analytical problems. In this section the main types of instrument will be discussed and examples given. A more complete review has been made by Beynon and Fontaine.[14]

At the present time, because of the very diverse nature of the instruments which may be classed as mass spectrometers, it is necessary to define the instrument in the most general terms. The one feature which all instruments have in common is that ionization and mass analysis take place in a high vacuum system. Briefly then, a mass spectrometer is a device which is capable of introducing a sample into a high vacuum and converting a proportion of the molecules in the resulting vapour into ions. The ions so produced are classified according to their mass to charge ratio (m/e) and the abundances of each ionic species is measured and recorded. As will be discussed in a later section, because such measurement and recording takes an appreciable interval of time, ion abundances must be detected as ion currents n_1/t. In order to give any significance to such ion currents, it is necessary to maintain a constant partial pressure n_{M} of the sample in the source and to keep a constant rate of ionization n_X/t. These considerations are unimportant in the design of a mass spectrograph, where only the masses of the individual ions are to be measured. These instruments, however, are comparatively rare.

The story of the development of the modern mass spectrometer is an account of continued efforts to improve the sensitivity of the machine, to increase its ability to distinguish between ions of closely similar mass, *i.e.*, its mass resolution ($m/\Delta m$) and to decrease the time taken to record the magnitude of the ion currents, *i.e.*, the mass spectrum. At the same time there have been attempts to increase the range of the instrument both in the production of ions of higher m/e values and in the classification and recording of such ion currents.

180°-*Focusing instruments*

An ion moving with uniform velocity in a magnetic field at right angles to the plane of its motion describes a circular path provided that the magnetic field is constant and uniform. This principle was exploited in the earliest form of mass spectrometer described by Dempster[15] in 1918, and it is of considerable interest that an instrument of this type is still in an active stage of development today. Positive ions are accelerated in a potential gradient V and enter a uniform magnetic field H which is perpendicular to the direction of their motion. The ions of mass m aquire a velocity v and so have an energy given by $\frac{1}{2}mv^2 = \mathrm{e}\mathrm{V}$, where e is the electronic charge. The radius R of the circular path which the ions describe is then given by the equation

$$Hev = \frac{mv^2}{R}$$

On combination of these two equations the field and potential gradient requirements for an ion with mass to charge ratio m/e travelling in an orbit of radius R are given by

$$m/e = \frac{H^2R^2}{2V}$$

The uniform magnetic field has a focusing action equivalent to that of a cylindrical lens so that beams of ions issuing from a slit are brought to a focus after suffering a deflection of 180° to form a first-order image of the slit with ions of the appropriate m/e values for the given field strength and potential gradient. This system is thus direction-focusing so that it is not necessary to inject a parallel beam of ions into the magnetic field. On the other hand, it requires that all ions having the same m/e value should have the same velocity v, that is to say this is not an energy-focusing system. The resolution of this type of instrument depends upon the homogeneity of the magnetic field over the whole of the ion path, the stability of the ion-accelerating potential difference and the width of the entrance and exit slits. The optimum values for slitwidths are those in which a successful compromise is achieved between the increase in resolution obtained by reducing slitwidth and the accompanying reduction in sensitivity.

Before giving any actual values of mass resolution achieved by various instruments, it is necessary to make a satisfactory definition of the term $m/\Delta m$. The original definition used by Dempster is expressed in the formula

$$m/\Delta m = R/(S_1 + S_2)$$

where S_1 and S_2 are the entrance and exit slitwidths. This makes the assumption that a perfect image of the entrance slits is formed in the plane of the exit slit and that the adjacent beams of ions are resolved when one image occupies the exit slit while none of the ion current due to the adjacent image enters the exit slit. Owing to imperfections of the experimentally attainable ion optics system, this simple equation cannot be retained as an adequate definition of mass resolution. The image will be distorted, having chromatic aberration due to variations in the kinetic energy of ions of the same mass and would have "wings" on either side due to the gas scattering in the ion path. These aberrations are taken into account by assuming a constant β such that the effect of the aberrations is shown to be proportional to the radius of curvature of the ion path as in

$$m/\Delta m = R/(S_1 + S_2 + \beta R)$$

Despite the obvious value of this equation it is more common to apply an empirical definition of mass resolution in which unit resolution is said to be achieved when there is a valley between adjacent peaks in a mass spectrum record. The peaks should be of equal height and the depth of the valley is chosen arbitrarily; the height of the valley above the base-line is expressed as a fraction of the peak height. When comparing the advertised performance of commercial instruments or the published figures for mass resolution of experimental instruments, it is important to identify the criterion which has been applied for unit mass resolution, as this can range over two orders of magnitude. Alternative criteria for resolution which have been suggested are based on peak width or contribution to a mass peak from an adjacent peak of the same height. The effect of slitwidth on mass resolution in a modern 180°-focusing mass spectrometer is illustrated in Fig. 6 which shows a mass spectrum for krypton recorded with slitwidths of 0·25 and 0·50 mm.

The stability and simplicity of this method of mass selection has led to its adoption and development in a range of low-resolution instruments. In particular, Associated Electrical Industries have produced a number of commercial instruments under the generic name of M.S. 10 and 20, based on a design with a radius (*R*) of 5 cm. These instruments are still in a state of active development and improvement. The original design used a large permanent magnet with a field strength (*H*) of 1840 gauss. Scanning of a mass range of 1–200 was achieved by varying the accelerating voltage (*V*) either continuously or in steps. The resolution which could be achieved with a slitwidth of 0·50 mm was 40 with a 2% peak valley between adjacent peaks of equal height. This type of instrument is suitable for use as a sophisticated ionization gauge, when it may be bolted directly to the vacuum system being monitored. Alternatively, it may be used for leak testing, by using a gas with a characteristic mass spectrum as the test gas for tracing the leak in a vacuum system. The resolution is adequate for the identification of most of the residual gases found in high-vacuum systems.

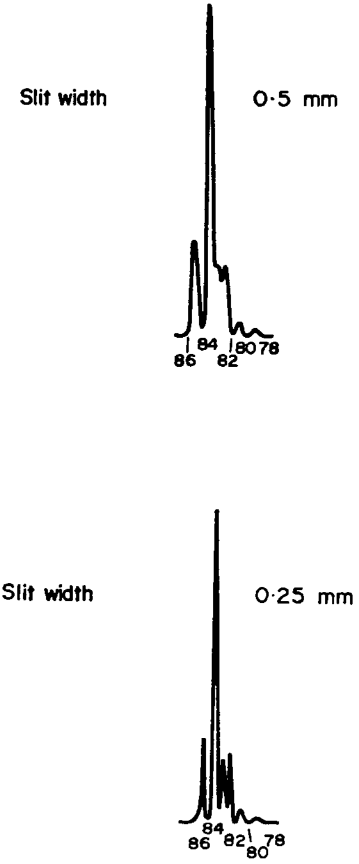


FIG. 6.—Effect of slitwidth on resolution: mass spectrum of krypton.

Recently, this design has been modified so as to convert the instrument into a versatile mass spectrometer for low-resolution general analytical studies. The mass range has been extended to 1000 by replacing the permanent magnet with a large electromagnet capable of providing fields up to 11,000 gauss. The resolution has been increased to approximately 550 by reducing the slitwidths to 0·025 mm and increasing the detector sensitivity. This design is particularly flexible since it permits the magnetic field to be swept at a number of alternative accelerating potentials.

The same company also produced a greatly simplified design in the Minimass Partial Pressure Gauge. The radius has been reduced to 1 cm and a small permanent magnet with a field strength of 4000 gauss is employed. Voltage scanning up to mass 240 permits the identification of each mass on a linear scale and the mass resolution is approximately 28 with 50% peak valley between adjacent peaks. This inexpensive compact model is intended for monitoring vacuum systems.

Similar models to the M.S. 10 range have been produced by the Atlas Co.* of Germany ($R = 28$ mm, $H = 2750$–4000 gauss, $m/\Delta m$ 18–44) and the Consolidated Electrodynamics Corporation of the U.S.A. ($H = 800$–6000 gauss, $m/\Delta m$ up to 600 with an electrostatic slit).

The chief advantage of the 180°-focusing system has been its comparative simplicity and consequent low price. The chief disadvantage in the past has been the necessity to scan the mass range by adjusting the ion-accelerating potential (V) so that ions are collected with varying efficiencies, the heavier ions requiring low potentials. Thus the sensitivity is lowest for ions with the highest m/e value and since in general such ion currents will give the most information from an analytical point of view, this reduction in sensitivity is a disadvantage. The recent substitution of large pole-face area electromagnets for the conventional permanent magnet has eliminated this disadvantage, permitting magnetic scanning. Although there is a corresponding rise in cost, the resulting flexibility has made this type of instrument the most important of the low-resolution magnetic series. The limiting factors in any further improvement of performance with this type of machine are the mechanical difficulties associated with providing source slitwidths of less than 0·025 mm and the resulting problem of providing additional detector sensitivity.

Sector field instruments

It was shown in 1940 that the phenomenon of the focusing of ion beams by causing deflection through 180° in a homogeneous magnetic field was in fact a special case of focusing by means of an inhomogenous field.[16] The ion beam should leave and enter the magnetic field at right angles to the field boundary and inside the field the ion describes a path which is a sector of a circle. The angle subtended by this sector may be 60°, 90° or in the limiting case above, 180°. The separation of ions of different mass to charge ratios takes place in an exactly analogous manner and beams of ions from the source situated some distance from the field boundary are brought to a focus at a collector symmetrically disposed on the other side of the sector magnetic field. The disadvantages of this type of geometry are the long path with consequent greater probability of collisional scattering, and the difficulties associated with the precise alignment of the sector magnetic field to obtain satisfactory focusing. On the other hand, there are considerable advantages in having both source and collector in

---

* Now Varian Mat.

field-free regions. The source is more readily accessible so that a variety of modifications may be carried out and the collector may be fitted without difficulty with an electron multiplier to increase detector sensitivity.

The most successful machine of this type was first introduced by the Metropolitan-Vickers Company (now G.E.C./A.E.I.) just before 1950. The M.S. 2 was a 90°-sector 15-cm radius instrument issued originally with a mechanically adjustable collector slit providing a maximum resolution of about 300. This resolution was later doubled by the use of a collector slit having an effective width which could be altered by giving it a high positive potential. For quantitative studies the collector slit was set at 0·62 mm to give a lower resolution but increased reproducibility, the record being in the form of a series of flat-topped rather than pointed mass peaks. A greatly improved version using the same basic geometry with a 90° sector of radius 15 cm was the M.S. 2H. The addition of an electron multiplier at the collector provided increased sensitivity, permitting a further increase in resolution to above 650. The mass range with the normal accelerating voltage of 2 kV was extended to 650 by increasing the magnetic field.

There have been a number of variations on this type of instrument, the most notable being the Atlas CH_4 with a resolution in excess of 1000.

A further stage in the improvement of the performance of the 90°-sector field instrument was provided by the A.E.I. M.S. 12 design in which the radius of curvature had been increased to 30 cm. A further decrease in slitwidth to 0·0125 mm was made possible by increasing the ion accelerating potential to 8 kV and with an electron multiplier detector a mass resolution of 7500 was achieved. In this design, which is now obsolete, both magnetic and voltage scanning facilities were provided, the latter permitting a mass spectrum to be displayed in less than 1/5 sec.

Double-focusing instruments

A beam of positive ions may also be analysed according to the velocity which the ions have attained. This velocity is proportional to the square root of the mass, provided that all the ions have suffered the same acceleration in a potential gradient, and velocity analysis is normally achieved by passage through transverse electrostatic fields. The principle of combining velocity and mass analysis to provide instruments having both direction and velocity focusing of beams of ions was discussed by a number of mass spectrometrists but little progress was made until Mattauch and Herzog[17] formulated their theory of double focusing, employing a radial electrostatic field for which $R\,dV/dR =$ constant where R is the radius and V the potential, and there is a homogeneous sector magnetic field. The improvements in the definition of the ion optic image made possible by the application of this principle stimulated the construction of a number of double-focusing instruments, culminating in the commercial development of two different types.

The first of these commercial double-focusing mass spectrometers was described in 1958 by Craig and Errock.[18] It was based upon the geometry suggested by Nier and Johnson[19] and was marketed as the first instrument specifically designed for the qualitative analysis of organic compounds. The commercial version became the A.E.I. M.S. 9 mass spectrometer.* It combined a magnetic sector of 90° with a radius

---

* Similar instruments have been developed by the Hitachi Organization in Japan and marketed by Perkin–Elmer.

of 15 cm, with an electrostatic analyser of radius 18·25 cm. A source slitwidth of 6·25 μm was used to give a resolution of 10,000. The instrument had the novel features of oscilloscope peak-matching, by which the precise masses of known and unknown ions were compared, with an accuracy sufficient to permit the identification of the atomic constitution of the unknown ion provided it had a mass of about 200. A further feature was the ability to record the spectra of compounds of low volatility by direct sample insertion into the ion source. There has been a steady improvement in the performance of the double-focusing instrument over the past ten years and the most recent models have a magnetic sector of 30 cm radius and an electrostatic sector of 38 cm radius with a source slit that can be reduced to 0·1 μm to give a resolving power of 100,000. At lower resolving powers the scan duration can be reduced to 2 sec. Additional features have included combined electron bombardment, field emission and water-cooled sources to permit the study of labile organic compounds. With a spectrometer having these characteristics it is possible to determine the atomic constitution of almost all the ions normally responsible for the peaks in a mass spectrum. However, making a number of precise mass determinations by the peak comparison technique is time-consuming and the most recent development is to carry out these determinations automatically by the aid of a small computer. The output from the spectrometer is digitized and the centroid of each mass peak determined from a score of ion current measurements or by differentiation. The centroids of known and unknown peaks are then compared not in terms of accelerating voltage as in the manual technique, but in terms of time with the aid of a megacycle clock. The spectra may be stored on magnetic tape to be played back in analogue form or they may be printed out in the form of a table of atomic constitution and ion abundance.

Double-beam mass spectrometer

The most recent development in instrument design has been the production of a double-beam instrument by the A.E.I. organization (M.S. 30). The beams from two ion sources are bent so as to pass through a single mass-analyser system and then allowed to diverge to two separate detectors. With such an arrangement it is possible to compare the spectra of two compounds recorded at the same time on a single chart recorder. The spectra may be of known and unknown compounds, permitting direct chemical mass marking or matching of spectra. The two spectra may equally well be those of a single compound ionized and analysed under different conditions, e.g., high and low resolution or electron voltage. The operation of this instrument has been simplified so as to make it appeal to the routine analyst. The multiplicity of controls on older models has been replaced by a few interlocked push buttons.

Spark-source mass spectrography

In the double-focusing high-resolution mass spectrometers described above, the deflection due to the electrostatic and magnetic sectors is in the same sense. In an alternative geometry, ion optic image corrections and double focusing may also be achieved if the two deflections have opposite senses.[20] In addition to providing high resolution, this geometry has the further advantage that all ions are brought to a focus in one plane. The result is that a complete mass spectrum may be recorded simultaneously by placing a photographic plate in this plane. These features were exploited successfully in instruments produced by the A.E.I. company in this country and the Atlas Co. in Germany. The ability of the double focusing system to accommodate ions with a large spread of kinetic energy made it possible to use an instrument for elemental analysis in which the ionization was carried out with a high-frequency spark. In the A.E.I. M.S. 7 the substances to be submitted to elemental analysis were incorporated into carbon electrodes if they were themselves non-conducting and submitted to the action of a high-frequency spark in the ion source region. The resulting vapour was then ionized and the ions submitted to mass analysis. Detection was by means of a photographic plate which not only permitted the simultaneous recording of ion currents at all masses but also compensated for variations in spark intensity by integrating ion current with time. The final measurement of ion abundance was made by developing the plate and measuring the density of the appropriate line. Comparisons with standards permitted quantitation of the technique and made it a competitor to emission spectrography. The great advantage of spark-source mass spectrometry is its ability to give a quantitative analysis of a large number of trace elements at the same time with only a few exposures. The limit of detection is very much lower than that of any other technique except activation analysis. Limits of detection of 1 in 10^9 are frequently quoted and the sample size may be as small as 50 mg.

While this type of instrument is eminently suitable for photoplate detection, the plate can be replaced by a slit and the ion current detected electrically. The spectrum may be scanned past the slit as in other instruments. This versatility has been made use of in designs developed by the Atlas company, who have marketed models which can be used with either electron bombardment or spark sources and with either photographic or electrical detection.

Mass filters

There are three types of non-magnetic mass analysers which can be classed as mass filters, that is devices in which radiofrequency fields are used to selectively exclude ions from a detector; they are classed according to their electrode systems and have been given the names of the quadrupole, the monopole and the three-electrode mass filters.

The quadrupole system consists of four rods which are mounted along the direction of the ion path between the ion source and the collector. The ions enter the space between the rods where they experience a radiofrequency field. Paul was the first to describe such an arrangement and in his design the rods were collinear and symmetrically disposed around the ion path, with opposite pairs being interconnected.[21] The potentials applied to the rods are as follows

$$V_x = U + V \cos \omega t$$

and

$$V_x = -V_y$$

where V is the amplitude of an RF sinewave of frequency ω, U is a superimposed d.c. voltage and x and y are planes at right angles to the ion path. Theoretically the rods should have a hyperbolic cross-section; in practice, with the exception of the instrument marketed by Industrial and Technical Equipment Co. Ltd., the cross-section is circular, and it is usual to make the distance between opposite pairs of rods smaller than the rod diameter by a factor of 1·16.

Under the conditions that $U/V < \frac{1}{6}$ for a given value of the RF amplitude V, only ions within a very small mass range can execute stable trajectories along the length of the rods and escape to the detector. All other ions have unstable trajectories which end in a collision with the rods. In order to scan a mass spectrum either the frequency or the RF amplitude V may be swept and for wide scans a combination has been preferred. Rods are about 20 cm long and 0·6 cm in diameter, so the assembly provides a very compact mass analyser. The upper frequency range is determined by power requirements and is about 5 MHz. The great advantage of this type of analyser is that it is insensitive to variations in ion energy, so quite crude sources can be used. On the other hand, it has the disadvantage of requiring very precise rod alignment and stability, of the order of a few thousandths of a centimeter. The power supplies must also be very stable and for the highest resolution the U/V ratio must be kept constant within at least 1 in 20,000. The first commercial mass filter was produced by the Atlas Co. in Germany in 1963. It has a resolution of 100 and a mass range of 2–100. More elaborate instruments have been produced by the E.A.I. Co. and most recently by the Finnegan Instrument Corporation. The latter organization has produced the mass filter with the highest performance, it being capable of scanning up to a mass of 750 with a resolution of 1000. Other instruments with more modest performances have been introduced by GEC/AEI, Vacuum Generators, Baltzers, 20th Century Electronics and Varian. The ability of the mass filter to scan a wide mass-range in a very short time interval has been exploited in the mass spectrometer/gas chromatograph combination described later. While in theory very high resolutions are accessible with the mass filter, at present it is in the stage of being an inexpensive low- and medium-resolution device having the virtue of rapid scan and small size.

The monopole

It was first pointed out by von Zahn that one quarter of the geometry of the quadrupole could be replaced by a single rod and a grounded electrode with a right angle cross-section.[22] The operation is the same, both RF and d.c. voltages being applied to the rod and scanning achieved by sweeping either the RF frequency or amplitude. As in the case of the quadrupole, the monopole suffers from the disadvantage of giving spiked peaks rather than the flat-topped peaks produced by magnetic sector instruments. On the other hand the monopole has the advantages of providing spatial separation of ions so that it is feasible to record several ion currents at the same time. In addition, the stability requirement of the U/V ratio is greatly reduced so that simple power supplies can be used while good resolution can be achieved without the same mechanical requirements. The chief disadvantage of the design is the sensitivity to contamination by particulate matter, which causes peak splitting, while small changes in the operating conditions may introduce large variations in the relative intensities of the ion currents. Nevertheless, a successful monopole partial pressure gauge *i.e.*, a low-resolution monopole, has been marketed by Veeco Instruments Ltd. It has a mass scan of 1–200, a resolution of 50 and a minimum detectable total pressure of 5×10^{-9} mm Hg.

The three-electrode analyser

This was first described by Fischer.[23] It is a very compact arrangement, each electrode being part of a hyperboloid of rotation. In practice this amounts to a ball-bearing being placed above and below a ring of the same cross-section. It will be at once realized that the quadrupole and three-electrode assemblies have the same cross-section geometries but the latter is in fact a three-dimensional device so that ions cannot escape from a field between the electrodes once they have entered it. The ions circulate continuously around the axis of the field, unstable ions being lost as before by collision with the electrodes. The stable ion current is detected by means of the inductive load which it presents to an external oscillator. High sensitivity has been obtained for the three-electrode system in experimental models, which have detected as few as 10,000 ions. There is also the possibility of storing ions for relatively long periods and hence integrating weak ion currents.

Time-of-flight mass spectrometers

In the time-of-flight mass spectrometer first described by Stevens[24] the ionizing electron beam was intermittent rather than continuous. The electron pulse lasted about 0·1 μsec and the time of a complete cycle was about 100 μsec. The ions formed during the pulse were accelerated into a drift tube which they traversed on their way to a detector. The rate of travel was inversely proportional to the square root of the mass to charge ratio, and with sufficiently good time resolution of the signal obtained from the detector it was possible to isolate the individual pulses produced by the separated bunches of ions. An oscilloscope was the most suitable means of displaying such a spectrum, provided that the time-base was coupled to the pulsing circuits. The original designs were rather insensitive but later instruments stored ions in the source for a few μsec before initiating the analysis, and commercial instruments such as that manufactured by the Bendix Co. have sensitivities which are comparable with those of other instruments. While repetition rates as high as 100,000 per sec at resolutions approaching 1000 are possible, it is important to stress the fact that the dynamic range under such conditions is low and good analytical operation is only possible by integration over some hundreds of cycles.

The great advantage of this type of mass analyser is the simplicity of the source and non-critical nature of the source and flight-tube geometry. Apart from the ability of the detector circuits to resolve smaller and smaller time intervals the only way of increasing the resolution of time-of-flight instruments is to increase the length of the path between source and collector. In order to prevent the size of the drift tube becoming unmanageably long the ions may be constrained by magnetic fields to move in a helix. A device of this type was recently described under the name of the Spiratron.[25] It is interesting that under these flight conditions the more energetic ions move in longer paths and arrive at the detector later, thus providing the possibility of a two-stage instrument. In this a helical path is coupled with a straight path in which the more energetic ions arrive first, thus eliminating the reduction in resolution caused by energy spread of the ion beam.

APPLICATIONS

Coupling with the gas chromatograph

The advantages of the direct coupling of the effluent of a gas chromatographic apparatus with the inlet system of a mass spectrometer were outlined in the introduction. The methods of carrying out the combination are discussed briefly here; for a more detailed discussion the reader is directed to earlier reviews.[26,27] There are two problems associated with such a combination, the first being the necessity of recording the mass spectrum during the period in which the sample is emerging from the base of the chromatographic column. This time may vary from about 10 sec to above 1 min, but during this time, in which the signal is rising and falling on the chromatograph detector, the concentration of the sample in the effluent carrier gas stream is rising and falling also. It is advantageous to record the mass spectrum with a constant sample pressure since otherwise the relative intensities of the ion currents will not be constant and the matching procedure referred to earlier will not be possible. For these reasons it is important to record the spectrum in a fraction of the time required for the whole of the sample to emerge and to make this record when the concentration is at its maximum. (Or alternatively to use a normalizing procedure based on a total ion-current measurement.) It is easier to change the accelerating voltage rapidly than to alter the magnetic field, and in many simple combination instruments the mass decade can be scanned in a second or less. Recent advances in instrumentation of magnetic instruments have made it possible to scan a mass decade magnetically in about 2 sec. This eliminates the disadvantage (associated with voltage scanning) of the lower efficiency of collection of the heavier ions. Much faster times of scanning are available with non-magnetic instruments and no problems are encountered with their use, for these reasons. A rapid scan allows the experimenter to examine partially resolved chromatographic peaks by recording the mass spectrum at the beginning and end of the chromatographic peak. In these spectra the role of the two sample components in the two spectra will be revealed.

The second problem associated with the direct coupling of the two instruments is the carrier gas. Even when the sample is at its highest concentration in the carrier gas effluent from the column, it is still present as only a small fraction of the carrier gas concentration. The direct admission of the carrier gas stream to the ion source would therefore result in the production of a high source pressure and in the recording of a mass spectrum which was largely that of the carrier gas itself. In order to overcome this problem it is necessary to achieve a segregation of the sample and to admit only it to the ion source, preferably without any loss of the sample. This ideal case has never been achieved in practice but there have been three successful compromises.

The first of these was developed by Ryhage and relied upon the effusion of the gas mixture from a narrow orifice for its separation.[28] The carrier gas used was helium and together with the sample the effluent passed through such a jet into a chamber at a reduced pressure. Immediately opposite to the jet was a small aperture leading to a second jet. The helium, because of its low gas density, had a high component of velocity at right angles to the line of flow and so collided with the chamber walls and was pumped away. The heavier sample molecules entered the aperture and issued together with a reduced amount of helium to the second jet where the process was repeated, the final aperture leading directly to the ion source and the second chamber being held at a pressure lower than that in the first chamber. Recoveries of the order of 50% of the original sample were achieved and the carrier gas concentration was reduced to 2%.

The second method also depended for its success on the exploitation of the low density of helium. The Watson-Biemann separator[29] allowed the effluent to pass into a tube made of glass frit or sinter. An outer jacket surrounded the frit and the annular space was continuously pumped out. The helium diffused through while the sample passed along the tube to the ion source. Recoveries of about 15% were achieved and the carrier gas concentration was reduced to a few per cent.

The third separator, which is now promising to oust all the others (although at present the majority use a glass frit separator) because of its cheapness and simplicity, was originally suggested by several investigators and is called the membrane separator. It uses a thin film of a polymer, usually silicone rubber, to divide the effluent stream from the ion source. The sample components are soluble in the membrane and diffuse through it into the ion source while the carrier gas is excluded. To eliminate memory effects and to increase the rate of diffusion and hence the response time, the film must be made as thin as possible. The recovery can be as high as 25% and the residual carrier gas concentration as low as 5%. All three separators are usually heated in order to increase the rate of the separation process and to reduce adsorption. There are a number of commercial instruments sold as a gas chromatograph–mass spectrometer package. The first successful design was the LKB 9000 which used the Ryhage separator, had a resolution of about 1000 and required a total sample size of only 0·1 μg. The GEC/AEI Co. used the glass frit separator in their M.S. 12 which in its final stages of development had a resolution of 7500 and required a sample size of only 2 μg. The M.S. 12 has now been replaced by the M.S. 30 double-beam instrument described previously, which uses a membrane separator. Lower resolution magnetic sector combinations have been developed by Edwards High Vacuum Ltd., and Vacuum Generators Ltd. The GEC/AEI Co. have combined their 180°-focusing instrument (the M.S. 20) with a gas chromatograph. The rapid-scan facility and low cost of the quadrupole mass filter have made it an attractive gas chromatograph detector and the EAI Co. and the Finnegan Instrument Co. in the U.S.A. have manufactured competitors to the magnetic instruments, using both frit and membrane separators. The resolution is in the 500–1000 range and the sensitivity is 3×10^{-11} g/sec. They have a very high scan-rate and indeed the scan-rate of all the instruments described is sufficiently fast to permit oscilloscope presentation of spectra. This is a useful facility because whether chromatographic peak detection is made by an external detector or by the ionization facilities of the instrument operating at an electron voltage below that of the ionization potential of the carrier gas, no peak identification is possible until the spectrum is run. The use of the oscilloscope obviates the need for the recording of unrequired mass spectra merely for peak identification purposes. In an analysis of a complex sample mixture this could be a costly undertaking.

The determination of isotopic constitution

The examination of any mass spectrum of an organic compound immediately reveals the polyisotopic nature of naturally occurring carbon, sulphur, chlorine, bromine and boron. The small proportions of the heavier stable isotopes of hydrogen, nitrogen and oxygen are less obvious. All these isotopes are stable and should not be confused with artificially produced radioactive isotopes such as carbon-14. The very great success of labelling techniques based on radioactive isotopes may be shared to some extent by the use of artificially enriched stable isotopes. The ability of the mass spectrometer to detect stable isotopes can never be as great as the ability of the counter to detect radioactive isotopes, but the great advantage is that the stable isotopes may be handled with none of the precautions inherent in the handling of radioactive compounds. The principles involved in tracing with stable isotopes are, however, exactly the same, the change in the isotopic constitution of samples (drawn from a dynamic or reacting system) being assayed by the mass spectrometer, and the signal at the abnormal isotope peak being analogous to the signal derived from the counter.

There is, however, a further advantage in the mass spectrometer method, because the ionization is followed by a dissociation process in which the labelling atoms are combined with fewer and fewer of the other atoms in the molecule. Thus an examination of the spectrum can give information not only on the extent of labelling but also on the position of labelling within the structure. In order to do this of course it may be necessary to use all the techniques which have already been outlined in previous paragraphs, such as precise mass determination.

If now the spectra of the labelled and unlabelled molecules are compared and the atomic constitution of the fragment ions is determined, it will be seen that the labelled atom is concentrated in one part of the molecule. This of course can only be achieved when the label atom is part of the backbone of the molecule. As has been observed earlier, hydrogen and deuterium atoms are notoriously labile in the ions and it is difficult to draw any but statistical conclusions from such labelling. This determination of the site of introduction of the label atom depends upon the ionization of a compound sufficiently volatile to permit evaporation into the source of the mass spectrometer. In some cases, because of the complexity of the reaction mixture or the intractable nature of the products, it may not be possible to make such a determination. It may still be feasible to get tracing information by conversion of the reaction mixture or some part of it into a volatile product which contains the stable isotope. In the case of carbon-14, radioactive tracing of the labelled compound is achieved by conversion into carbon dioxide or even methane. A similar conversion may be carried out with compounds containing carbon-13 and the ion current at $m/e = 45$ used as a measure of the total carbon-13 content. In a similar way the nitrogen-15 content of, for example, excreted urea, may be determined by Kjeldahl digestion followed by a hypobromite treatment to release molecular nitrogen. The ion current at $m/e = 29$ is a measure of the enrichment of the sample. Oxygen-18 may be assayed by pyrolysis followed by the oxidation of the carbon monoxide to carbon dioxide. The ^{18}O concentration is measured at $m/e = 46$. The precision of these measurements can be quite high and is improved by integrating the results of a number of measurements. The sensitivity depends upon the dynamic range of the instrument and can have a value of 0·01 atom %. When determinations of the isotopic concentration of both carbon and nitrogen are required the mass spectrometer may be connected directly to a conventional C, H, N analyser.

The very great advantage of the stable isotope method of tracing is that quite highly labelled material may be fed to experimental animals or patients without fear of the side-effects arising from the administration of similar doses of radioactive material. With the increasing availability of compounds labelled with ^{13}C, ^{15}N and ^{18}O and the wide distribution of moderately priced instruments capable of analysing them, a large increase may be expected in the use of stable isotope tracing in the biochemical and medical fields.

Quantitative analysis

With an ion source with a constant ionizing electron beam current and with a constant source pressure of the sample gas it is possible to determine the sensitivity of an instrument for any particular substance. Since in general any substance will produce ion currents at a number of different m/e values the sensitivity at any one of these values may be chosen. In the absence of any reason to the contrary the value chosen will be that at which the most intense ion current is produced, that is to say the m/e value corresponding to the highest peak in the mass spectrum. It is however difficult to record the pressure of the sample vapour in the ion source by any other than some form of ionization gauge, because of the very low pressures involved. It is therefore common practice to establish a constant flow of sample vapour through a capillary or sinter into the ion source from a reservoir of the sample gas maintained at a higher pressure. The sample pressure in the reservoir and hence the pressure in the ion source remain substantially constant during the time in which measurements are made. Once the instrument has been calibrated by measuring the sensitivities on selected m/e values for pure sample vapours the analyst is in a position to deal with any mixture of those compounds for which he has recorded sensitivities. For every component in the mixture the analyst must measure the intensity of one ion current or peak height in the mixture spectrum. While it is sometimes possible to calculate the mixture composition by a spectrum-stripping technique, a more general method is to express the values of the ion currents or peak heights as sums of the products of sensitivities and partial pressures, obtaining a series of linear simultaneous equations and to invert the matrices. For complex mixtures this is best carried out by computer. It is sometimes impossible to carry out this routine because the resolution of the instrument is not sufficient to enable separation of ion currents at closely similar m/e values. If this is the case then a solution to the problem is to record two spectra of the mixture, one before and one after the quantitative conversion of one of the components of the mixture into a second substance. As an example the masses of carbon monoxide and nitrogen differ only by 1 part in 2800 and if the instrument available cannot achieve this resolution then a low-resolution spectrum is recorded and then the sample vapour in the inlet system is exposed to iodine pentoxide which converts the carbon monoxide into carbon dioxide quantitatively. A second spectrum is then recorded and in this spectrum the ion current at mass 28 is due only to nitrogen. From a comparison of the two spectra the concentration of carbon monoxide can be deduced.[30]

Analyses such as those described can only be carried out if a few milligrams of the sample are available and if the sample is sufficiently volatile to permit the achievement of suitable reservoir pressures. Much modern mass spectrometry is carried out, however, with solid samples of low volatility and these are normally analysed by introducing them directly into the ion source on the end of a ceramic or glass probe which is inserted into the instrument through a vacuum lock and within a few mm of the ionizing electron beam. In the most recent developments the probe may be heated or cooled to control evaporation. The resulting vapour molecules move only a short distance before they become ionized and so substances with extremely low vapour pressures may be analysed. Under these circumstances the sample pressure within the source is controlled only by the rate of evaporation and can only be adjusted crudely by altering the temperature or the position of the sample. It is thus not easy to calibrate the instrument or to analyse quantitatively. Further, since sample sizes have tended to diminish, the sample pressure may vary widely during evaporation, owing to the exhaustion of the solid on the probe. For this reason an alternative system has been devised in which the ion current due to the sample is integrated while the whole of a known amount of the sample is being evaporated. It is then possible to relate the integrated ion current to the amount of sample evaporated and to determine a sensitivity for the instrument with that sample.[31] One method of doing this would be to scan the whole mass spectrum repetitively at as rapid a rate as possible, while evaporating the sample, and to measure the corresponding peak height on each scan and plot peak height against time for each significant *m/e* value. This is possible experimentally and Fig. 7 shows the results of such a determination, using 60 ng of *p*-tyramine as the sample. The total evaporation time is about 100 sec. However, the recording of a large number of spectra is an expensive process and measurement of the spectra is tedious. The system only becomes practical if the mass spectrometer output is digitized and stored either on tape or in a core for processing by computer.

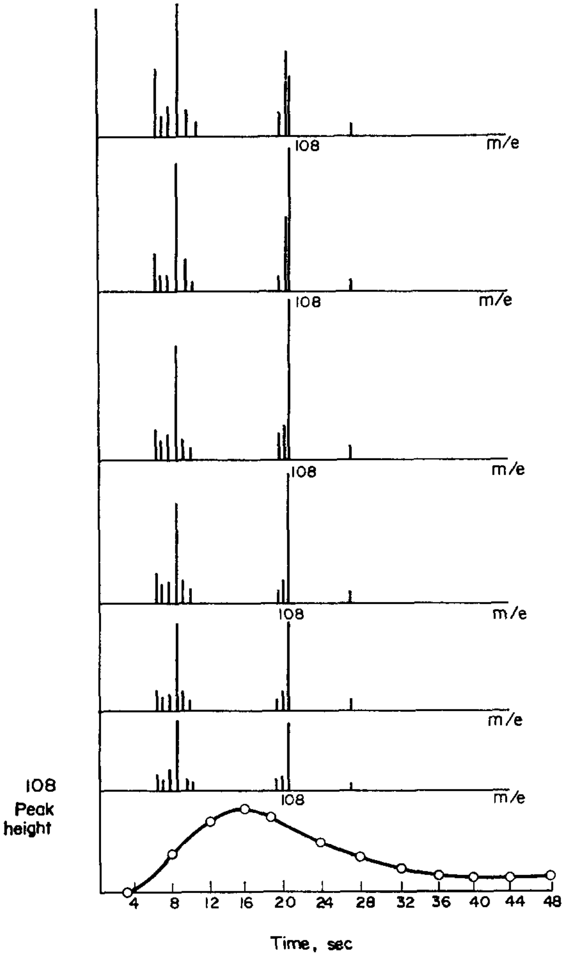


FIG. 7.—Mass spectrum scanned at 8-sec intervals during the evaporation of 60 ng of *p*-tyramine.

However, a compromise may be made in which not all of the spectrum but only a small part of it is repetitively scanned during the course of evaporation. The simplest possible situation is when only one ion current is recorded, for example the molecule ion-current since that will give most information about the molecule, although the argument would apply with equal force to a characteristic fragmentation peak in the mass spectrum. If the instrument is tuned to the selected *m/e* value before the evaporation begins and the ion current is recorded during the whole course of the evaporation of a small sample, then the record of the ion current at the selected *m/e* value is a measure of the rise and fall of the sample vapour concentration in the ion source, and the area under the curve so obtained is directly proportional to the integrated ion current and hence to the weight of sample evaporated. Thus an inexpensive and greatly simplified record is obtained and computer analysis is unnecessary. The problem of tuning in to a specific *m/e* value before an ion current is established at this value, *i.e.*, before evaporation has begun, is not always a simple matter. If voltage scanning, time-of-flight or radiofrequency instruments are being used, it is not too difficult, but with magnetic sector instruments without a very accurate mass-marking system it may not be possible to achieve. Further, it is often the case that an instrument of the latter type will go off tune during the course of an evaporation. For these reasons a system has been developed in which the single mass is repetitively scanned by means of peak switching facilities. Since this may be carried out in about 1 sec, only a short inexpensive recording is required and this consists of a series of peaks, the heights of which are proportional to the instantaneous ion current at the selected *m/e* value. These peaks rise and fall as the evaporation proceeds and it is the envelope of these peaks which constitutes the integrated ion current curve. Further, it is the area under this envelope which is proportional to the amount of sample evaporated. The problem of tuning to the *m/e* value with sector instruments may be solved by using a second calibrating substance in a second inlet system of the instrument, usually a reservoir of the type described above. The compound used is most commonly heptacosafluoro-tri-n-butylamine, which is allowed to flow into the source, and a peak in its spectrum is selected which is close to the *m/e* value which is being used for integration. This peak is then tuned in on the instrument by adjusting the magnet scan and the accelerating voltage is then altered so as to tune in the desired *m/e* value. The reference supply may then be cut off and evaporation initiated. If it is suspected that the sensitivity of the instrument is varying during the course of the evaporation then the ion currents due to the reference sample peaks may be recorded alternately with the sample peak currents. Any change in the height of the reference peaks would be due to a change in instrument sensitivity alone, since the sample source pressure of the reference compound is constant. In quantitative analysis by this technique the machine is first calibrated with known weights of pure samples of the compound. Comparison of the sample integrated ion-current curve area with the calibration graph gives a direct determination of the amount of unknown evaporated. Figure 8 shows such a calibration graph and it can be seen that there is linearity of response over several orders of magnitude. The limits of detection are very low indeed and detection of as little as 10^{-14} g has been achieved in favourable cases.[31] The effect of the matrix from which the sample is evaporated has been studied by making mixtures of two compounds, the major component being present in up to a million times the concentration of the minor component. It was found that provided the total sample size did not

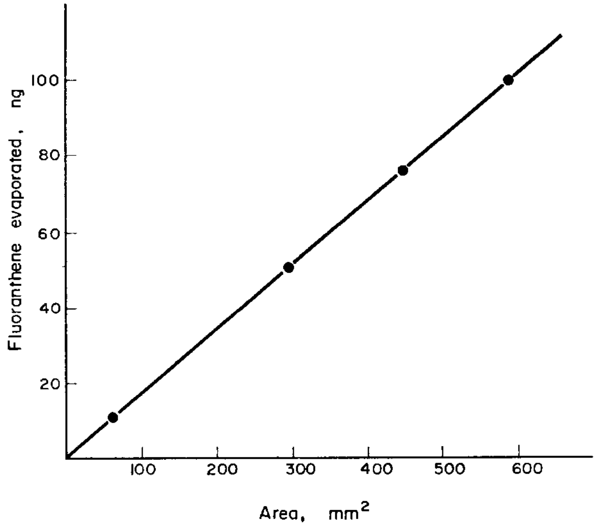


FIG. 8.—Calibration graph for fluoranthene.

exceed 5 μg, thus ensuring that the ion source pressure did not rise above 10^{-5} mm Hg, a plot of the integrated ion-current curve area for a characteristic m/e value of the minor component was linear down to the detection limit. The sensitivity of this technique varies with the compound and also with the characteristic m/e value selected. While it may be felt that the molecule ion peak is the most characteristic in the spectrum this sometimes carries only a very tiny fraction of the total ion current and thus can only give a low sensitivity. In such cases a characteristic fragment ion peak may provide a suitable m/e value for integration.

The analysis of metals

The most efficient method of analysing for trace metals is by the use of the spark-source double-focusing mass spectrometer such as the A.E.I. M.S. 7. Although the accuracy is limited by photoplate detection the ion currents due to all the ionized species are recorded at the same time and a limit of detection of one part in 10^9 has been claimed. Where the analytical requirements are less stringent it is sometimes possible to use the integrated ion current method with a general purpose mass spectrometer. Some metal salts such as mercuric chloride are themselves sufficiently volatile to permit their evaporation into the ion source directly. Figure 9 shows a portion of the mass spectrum for mercuric chloride, including the molecule ion region. It can be seen that the isotopic complexity has resulted in the distribution of the ion current over a number of isotopic ions and the sensitivity is thus much lower than that which can be achieved for a monoisotopic substance. However, amounts of mercuric chloride down to 1 ng can be determined with an error of 5%.[32]

Where no simple salt can be prepared it is necessary to convert the metal into a volatile form by making a chelate such as the acetylacetonate. The volatile nature of such chelates was first demonstrated by Morgan[33] over 40 years ago and more recently their properties have been exploited in an elegant and extensive study by Sievers,[34] using gas chromatography. The volatility of many metal chelates is improved by

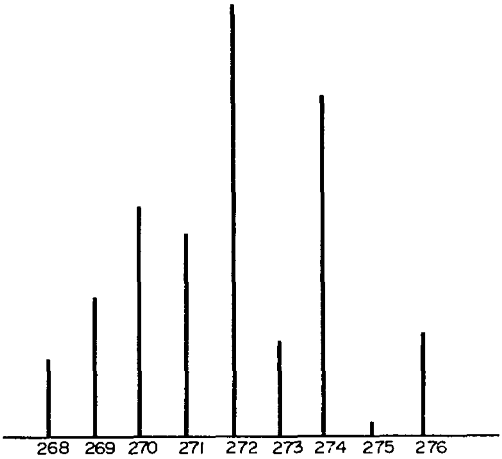


FIG. 9.—Mass spectrum of mercuric chloride.[31]

the substitution of fluorine and sulphur atoms in the diketone molecule. Although it is debatable whether alkali metal derivatives of diketones and keto esters can be classified as chelates, they may be evaporated from a probe into the ion source at temperatures below 200°.[35] Although it is possible to detect very small quantities of these compounds by the integrated ion current method the procedure is complicated by the fact that alkali metal chelates undergo two types of reaction upon evaporation—association and exchange.[36] Thus the mass spectra exhibit ions of the form $M_xL_y^+$ and the introduction of a large amount of a sodium chelate followed by, for example, a potassium derivative of a second diketone may result in the production of a spectrum revealing ions in which the two alkali metals have exchanged diketones. More complex association reactions are revealed if the chelates of alkali and alkaline earth metals are evaporated together.[37] Double chelates of the form $MM'L_3$ have been shown to exist. In the absence of the alkali metals however it is possible to estimate as little as 10^{-9} g of alkaline earth metals as their chelates with trifluoro-5,5-dimethylhexan-2,4-dione even though the mass spectrum exhibits polymeric peaks. Similar association reactions have been shown to occur between the chelates of alkali and rare-earth metals with the formation of binary chelates having the general formula $MM'L_4$.[35] In the absence of the alkali metals, however, very small quantities of rare-earth metals may be estimated as their chelates with heptafluoro-7,7-dimethyloctan-4,6-dione by the integrated ion current method.

1,3-Diketones or keto-esters have been used to make volatile derivatives of a number of other metals, the most volatile of these being the transition metal chelates, and detection limits for these species in the subnanogram range have been claimed. The power of the integrated ion current technique is, however, best demonstrated by the determination of mixtures of zirconium, hafnium and titanium as their trifluoroacetylbenzoylmethane chelates at the nanogram level–a formidable task by any other method.[39] There are many other chelating agents which form metal derivatives sufficiently volatile for their ready evaporation into the ion source and among these are 8-hydroxyquinoline, dipyridyl, dimethyl- and phenylglyoxime and the thio and amino derivatives of acetylacetone. A notable exception to this list is benzoylphenylhydroxylamine which forms derivatives which are not sufficiently stable to survive evaporation.

The integrated ion current method has been applied to the determination of a variety of organic compounds. It is perhaps very well suited to the analysis of polycyclic hydrocarbons obtained as air pollutants from automobile exhausts or the soot of smoky flames. The limit of detection for compounds such as the benzpyrenes is several orders of magnitude lower than that of any other technique. Further the spectrum of a complex mixture may be reduced to a number of molecule ion peaks by reducing the ionizing electron voltage to about 10 eV. Drugs have been assayed in blood and urine, and the distribution of non-catecholic amines in the human brain has been plotted.

A final feature of the integrated ion current technique is provided fortuitously by the differential rates of evaporation of closely similar compounds from the surface of a mass spectrometer probe. If the sample consists of a pair of isomers such as for example *o*- and *p*-nitrophenol, and if the curve is plotted for the molecule ion, then instead of the gaussian curve obtained for most sample evaporations a curve with two distinct maxima is obtained. This is because one isomer is being evaporated before the other. In all cases where isomerism can occur the integrated ion current curves have been shown to have fine structure. In the case of the chlorinated hydrocarbon "Chloran" no less than five maxima are visible. Structure has been demonstrated in curves obtained for *cis-trans* isomers, dioximes, polycyclic hydrocarbons, and very convincingly for metal chelates. By this means, the existence of *cis-trans* isomerism in the 8-hydroxyquinoline derivatives of bivalent metals has been demonstrated and complete separation of the isomers has been achieved in the 8-hydroxyquinoline derivatives of tervalent metals.[40]

An interesting application of the integrated ion current technique is in the assessment of the efficiency of decontamination agents and the cleaning of surfaces. For this application the probe is replaced by a small cylinder made of the material on which decontamination studies are to be made. The surface is then coated with a substance which is sufficiently volatile to be evaporated into the ion source at a high temperature. The amount adhering is determined in the normal way. The probe is then recontaminated and before assay is washed in the appropriate decontamination agent. The amount remaining is then assayed as before.

In the original study it was found that washing in cold solutions of efficient decontamination agent removed the contamination down to the level where it existed as a monolayer on the surface. This monolayer was only removed by treatment with the agent at elevated temperatures. More recently a phosphate-free decontamination agent, Decon 90, has been shown to break through the monolayer even in the cold and to leave no detectable film of contamination on the mass spectrometer probe after treatment at 50°.

Zusammenfassung—Es wird ein Überblick über die elementare Theorie, die Technik und die Anwendung der Massenspektrometrie gegeben. Besonders wird auf apparative Entwicklungen und dadurch bedingte neue Anwendungsmöglichkeiten hingewiesen.

Résumé—On a effectué une revue de la théorie fondamentale, de l'instrumentation et de l'application de la spectrométrie de masse, spécialement en ce qui concerne le développement de l'équipement et sa répercussion sur le cadre l'application.

REFERENCES

1. J. R. Majer, R. Perry and M. J. Reade, *J. Chromatog.*, 1970, **48**, 328.
2. J. R. Majer, W. D. Capey and J. C. Robb, *Nature*, 1964, **203**, 294.
3. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, Elsevier, Amsterdam, 1960.
4. F. W. McLafferty, *Mass Spectrometry of Organic Ions*, Academic Press, New York, 1963.
5. J. R. Majer, *Advances in Fluorine Chemistry*, Vol. II, p. 55, Butterworths, London, 1961.
6. B. G. Gowenlock, J. Kay and J. R. Majer, *Trans. Faraday Soc.*, 1963, **59**, 2463.
7. F. W. McLafferty, *Interpretation of Mass Spectra*, Benjamin, New York, 1966.
8. J. R. Majer and C. R. Patrick, *Nature*, 1961, **192**, 866.
9. J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1861.
10. K. R. Jennings, *Proceedings of Symposium on Some Newer Physical Methods in Structural Chemistry, Oxford, 1966*, p. 105, London United Trade Press, London, 1967.
11. H. D. Beckey, *Z. Naturforsch.*, 1959, **14a**, 712.
12. M. S. Munson and F. H. Field, *J. Am. Chem. Soc.*, 1966, **88**, 2621.
13. O. A. Koleoso, S. M. C. Dietrich and R. O. Martin, *Biochemistry*, 1969, **8**, 4172.
14. J. H. Beynon and A. E. Fontaine, *Instr. Rev.*, 1967, 470.
15. A. J. Dempster, *Phys. Rev.*, 1918, **11**, 316.
16. A. O. Nier, *Rev. Sci. Instr.*, 1940, **11**, 212.
17. J. Mattauch and R. F. K. Herzog, *Z. Physik.*, 1934, **89**, 786.
18. R. D. Craig and G. A. Errock, *Advances in Mass Spectrometry*, ed. J. D. Waldron, p. 66, Pergamon, Oxford, 1959.
19. A. O. Nier and E. G. Johnson, *Phys. Rev.*, 1953, **91**, 10.
20. H. Hintenberger and L. A. Konig, *Advances in Mass Spectrometry*, ed. J. D. Waldron, p. 16, Pergamon, Oxford, 1959.
21. W. Paul and H. Steinwedel, *Z. Naturforsch.*, 1953, **8a**, 448.
22. U. von Zahn, *Rev. Sci. Instr.*, 1963, **34**, 1.
23. E. Fischer, *Z. Physik.*, 1959, **156**, 1.
24. W. E. Stephens, *Phys. Rev.*, 1946, **69**, 691.
25. J. M. B. Bakker, *Proc. Intern. Conf. Mass Spectr.*, Brussels, 1970.
26. W. H. McFadden, *Advances in Chromatography*, ed. J. C. Giddings and R. A. Keller, Vol. 4, p. 265. Arnold, London, 1967.
27. D. I. Rees, *Talanta*, 1969, **16**, 903.
28. R. Ryhage, *Anal. Chem.*, 1964, **36**, 759.
29. J. T. Watson and K. Biemann, *ibid.*, 1964, **36**, 1135.
30. J. R. Majer, *Talanta*, 1970, **17**, 1970.
31. A. E. Jenkins and J. R. Majer, *ibid.*, 1967, **14**, 777.
32. J. R. Majer, *ibid.*, 1969, **16**, 420.
33. G. T. Morgan and F. H. Burstall, *Inorganic Chemistry, A Survey of Modern Developments*, Heffer, Cambridge, 1936.
34. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
35. R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, *Anal. Chim. Acta*, 1969, **45**, 305.
36. J. R. Majer and R. Perry, *Chem. Commun.*, 1969, 271.
37. *Idem*, *ibid.*, 1969, 454.
38. R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 471.
39. M. G. Allcock, R. Belcher, J. R. Majer and R. Perry, *Anal. Chem.*, 1970, **42**, 776.
40. J. R. Majer and M. J. A. Reade, *Chem. Commun.*, 1970, 58.

Talanta, 1972, Vol. 19, pp. 589 to 621. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW†

ANALYTICAL MASS SPECTROMETRY

J. R. MAJER
Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.

(*Received* 12 *July* 1971. *Accepted* 11 *November* 1971)

Summary—A review is made of the basic theory, instrumentation and application of mass spectrometry, with special reference to the development of the equipment and its impact on the scope of application.

THE IONIZATION PROCESS

ANALYSIS by mass spectrometry depends upon the segregation of ionized molecules in magnetic, electric or radiofrequency fields. The ionization process which precedes this separation must take place in the gas phase and this imposes certain limitations on the technique, which are discussed later. Mass spectrometry is best introduced by using its relationship to other physical techniques based upon ionization. The ionization process may be described most generally by the interaction of a species M, which may be a molecule, an atom or a free radical, with a second species X, which may be an electron, a photon, an ion, a fast molecule or even a high potential gradient. M may be considered to be in thermal equilibrium with its surroundings but X must have a certain minimal energy content (E) which is greater than the binding energy of the electron in the lowest energy orbital in M, *i.e.*, the lowest ionization potential (I) of M. As a result of this interaction the lowest-energy electron is ejected and an ion M^+ is formed. For cases in which E is greater than I the excess of energy will be partitioned between the ion (E_1) and the electron (E_2). As the free electron is so light when compared with even a small polyatomic ion, any translational energy released in the process will be almost completely retained by the electron, which can of course retain no other form of energy. The ion M^+ on the other hand, although it has no translational energy, may have excitation energy (E_1) which may be electronic, vibrational or rotational.

$$\begin{array}{ccccccc} M & + & X(E) & \rightarrow & \mathrm{M}^+(E_1) & + & e(E_2) \\ n_{\mathrm{M}} & & n_{\mathrm{X}} & & n_1 & & n_2 \end{array}$$

In order to examine the consequences of this interaction in a real environment we must assume an assembly of particles of species M, their number being n_{M}. The number of particles of species X, which will most normally be measured as a flux, is n_{X} and the numbers of ions and electrons produced will be n_1 and n_2 respectively. Except in the case of multiple ionization n_1 and n_2 will be equal.

There are obviously two ways of investigating the ionization process experimentally: either the number of ions or the number of electrons may be measured. Such measurements are most commonly made by collecting the charged species with electrode assemblies across which the appropriate potential gradients are applied.

---

† For reprints of this review, see Publisher's announcement near end of this issue.

It is most convenient to investigate ionization as a continuous process so that n_M is kept constant by maintaining a flux or current of X through the assembly of molecules, atoms or radicals M. The resulting numbers of ions and electrons may now also be measured as fluxes, *i.e.*, numbers of ions or electrons per second or, more familiarly, electric currents. Let us suppose that n_M and n_X are kept constant while E is varied. The electron current n_2/t (where t is time) is now measured, for example, by inserting a pair of polarized electrodes into the cell in which M and X are interacting. If the electron current n_2/t is plotted against the energy E, the result is a typical ionization curve with a very steep rise in n_2/t as E rises above the ionization potential of M. When X is a photon then E may be very sharply defined by the wavelength of X and the ionization potential may be measured with considerable precision. When X is an electron, E is not precisely defined, as it is not very easy to obtain a beam of monochromatic electrons of suitable intensity. As electrons are normally produced from a white hot tungsten or rhenium filament they retain a Boltzmann distribution of energy $\pm\Delta E$ which is an appreciable fraction of a volt. As a result the inflection in the ionization curve is less precisely defined and the value of the ionization potential less certain. Now let us consider an alternative experiment in which the energy E is kept constant and considerably greater than the ionization potential of M. Instead of the total ionization current n_2/t being measured, the energy distribution in the emitted electrons is determined. This may be achieved experimentally by interposing a retarding potential grid between the two collecting electrodes or more elaborately by passing a beam of the emitted electrons through a transverse electric field and dispersing them according to their velocity. A plot is now made of E_2' against n_2'/t where E_2' is the energy in any emitted electron and n_2' is the number of electrons having such a translational energy. Then $\sum n_2' = n_2$. The difference between the energy of the projectile (E) and the translational energy of the emitted electron (E_2') is equal to that energy retained by the ion M^+. When X is a photon of high energy, this curve may be recognized as the photoelectron spectrum. Such a curve will have several maxima corresponding to the ionization of electrons in orbitals of different energies. In addition, for simple molecules, the maxima may reveal structure due to the formation of the ion in a variety of excited states. This experiment gives information about the energies of orbitals in polyatomic molecules in addition to the lowest ionization potential. Similar information is theoretically available if X is not a photon but an electron. Once again however, there is the problem of the energy spread experienced with electron beams. Electron monochromators are now being developed, however, giving currents as high as 10^{-8} A with an energy spread of as little as 20 mV. Combinations of two of these devices have been used to provide determinations of the energy distribution of emitted electrons, and a new spectroscopic technique, electron energy loss spectroscopy, is being developed. Once again the information available with this technique is concerned with the energies of orbitals in simple polyatomic molecules rather than with structures.

The alternative method of investigating the ionization process is by measuring the ion current rather than the electron current. A plot of n_1/t against E once again provides a method of determining the ionization potential of M. The results are more precise when X is a photon rather than an electron but the measurement of ionization potentials from the ionization efficiency curves obtained with mass spectrometers is common practice and various extrapolation procedures and deconvolution devices are used to increase precision of the determination. When X is an ion, the situation is complicated by the involvement of the recombination energy of the projectile ion with an electron. This complication also arises with the other techniques mentioned above. A measurement of the ratio n_1/n_M gives a measure of the ionization cross-section of the molecule M. The ionization efficiency curve, which is a plot of n_1/t against E does not give any information about the higher ionization potentials of polyatomic molecules because it is not possible to identify the variation of cross-section with E for any specific ionization process in which an electron of particular energy is being removed, except in the simplest possible case of the hydrogen atom or possibly the hydrogen molecule. Energy analysis of the ion current reveals no information, because the translational energy is all removed by the electron and at present there is little or no possibility of the determination of the nature of the excited states of ions.

While however, little information of this type is available from an examination of the ion current, the technique of mass spectrometry is based on an alternative way of looking at the ion current. This arises because it is possible to segregate ions not according to their energy content but according to their relative mass. The various methods by which this segregation is achieved are discussed below and it is only necessary to point out that the assembly of the species M may now consist of a number of different molecules, atoms or radicals. Each of these will be converted into the appropriate ions M^+ and it is now possible to measure all the individual ion currents n_1/t and to plot n_1/t against the mass of the ion m. Such a plot constitutes a mass spectrum.

$$m \sum_{0}^{M} n_1' = n_1$$

If the assembly of species is, for example, a mixture of rare gases so that the only ionization processes possible were the production of the singly-charged rare gas ions then it is possible to analyse the mixture by mass spectrometry. Both n_M and n_X must be kept constant so that the rate of production of ions is constant. The individual ion currents of the species M are then proportional to the partial pressures of the species M in the mixture and the sum of all these currents is equal to the total ion current n_1/t. This situation is rather similar to the conditions of fluorescence analysis where the incident radiation is analogous to the electron beam and the fluorescent radiation is analogous to the ion beam, the wavelength and mass being characteristic of the species M. There are very few cases in which this very simple form of mass spectrometry has a modern application. There are two examples worth recording however, the first medical and the second cosmochemical. The most readily available gas mixture is the atmosphere and a mass spectrum of air readily reveals the separation of the ion currents due to oxygen, nitrogen, carbon dioxide and argon. The efficiency of a patient's respiration may be assessed by taking samples of the atmosphere from his lungs. This process can be carried out continuously and can show not only the state of the patient's breathing but also the concentration of any foreign gas introduced to induce anaesthesia.

The second application also deals with the analysis of atmospheres, but in extra-terrestrial situations. The development of very small light mass spectrometers, now referred to as "flyable" instruments, permits their transportation by rocketry to a number of remote situations. The molecule and ion concentrations in the outer layers of the earth's atmosphere may be examined by carrying a small mass spectrometer on a rocket and relaying the information which it gathers to a remote ground station by radio. An extension of this principle will allow the examination of a number of planetary atmospheres.

The dissociation of excited ion-molecules

The great value of mass spectrometry as an analytical technique does not derive from simple applications such as these, but from a quite distinct and separate result of the initial ionization process. For ionization to take place the energy in the electron must exceed the lowest ionization potential of the molecule. It must therefore have a value of E which is at least 15 eV since the ionization potentials of all molecules lie between 6 and 15 eV. It is common practice, in order to obtain sufficiently high values of the cross-section n_1/n_M which determines the sensitivity, to choose values of E in the 50–100 eV range. The cross-section n_1/n_M does not vary significantly above 100 eV but falls off rapidly below 50 eV. Although not all of the energy in the projectile electron is transferred to the molecule, the result of the ionization process may be the production of an ion with a considerable excess of energy (E_1). As the excited molecule ion is normally produced under high vacuum conditions (approximately 10^{-6} mm Hg) this excess of energy cannot be lost by collision with other molecules. It can thus only be reduced by the emission of a photon, a comparatively unlikely event, or by the molecule ion undergoing dissociation or rearrangement. As the bond dissociation energy of all chemical single bonds lies between 2 and 5 eV the transfer of a small fraction of the translational energy of the incident electron can result in the fission of a number of chemical bonds with the production of radicals and smaller ions. Because of the large excess of energy the dissociation process has two important features. The first is that there are a number of alternative modes of dissociation available and the diversity of these decompositions is further enhanced by the fact that the electrons have an energy spread $\pm\Delta(E)$ and may transfer a variable amount of their translational energy to the molecule, depending on the nearness of approach and the consequent intensity of interaction. As a result the excited molecule ion may dissociate in a number of parallel and consecutive reactions. If E is high, the molecule ion is most likely to react by breaking chemical bonds; if E is low the molecule ion is most likely to rearrange. The second feature is that the rate constants for the dissociation processes are very high and the reactions have negligible energies of activation. As a result the rates of reaction are almost totally unaffected by experimental parameters other than E. This means that the ratios of the ion currents for the molecule, fragment and rearrangement ions will have constant values over wide variations of n_M or n_X or the temperature of the ionization cell. The relative intensities of the ion currents, which are responsible for the peaks in a mass spectrum, constitute what has come to be known as the cracking pattern of the molecule. It is the cracking pattern which is therefore substantially invariant and constitutes a fingerprint of the molecule in the same way that the infrared absorption spectrum does. It is thus possible to match the cracking pattern observed with a chemical compound measured upon one instrument with that of the same compound measured on a machine with a completely different geometry. This match is not as complete as that obtained with infrared or NMR spectra, but the usefulness of this near identity has led to the collection both privately and by industrial and government organizations of large libraries of mass spectral cracking patterns. The best known collection of spectra has been made by the American Petroleum Institute Research Project 44. A second rapidly growing collection is being amassed by the Mass Spectrometry Data Centre situated at Aldermaston. The reduction of these cracking patterns to digital form permits a direct comparison by computer, and several schemes are in operation by which the mass spectrum of an unknown compound may be compared with a library of the spectra of known compounds, held upon a disc in a computer memory.

One of the most severe problems encountered in the matching of spectra is the necessity of matching the purity of the standard and unknown samples. The presence of a substantial impurity in either may cause a mismatch so severe that the identity is lost. The effect of the minor constituent in distorting the mass spectrum may be further magnified by a difference in the rate of evaporation of the two components. With volatile samples this effect may be minimized by evaporating all of the sample into a reservoir from which the vapour flows into the ion source. When solid samples are being introduced into the source by the insertion-probe technique this is not possible. The situation is at its worst when isomers are being studied. There are only very small differences in the mass spectra of structural isomers and it is only possible to match the spectra of unknown and standard if the purity and method of sample admission are kept the same. Fortunately, there are two ways of dealing with this problem. The first is to use the technique of differential evaporation as discussed in the section describing quantitative methods, and the second is to combine mass spectrometric identification with some other technique of physical separation such as chromatography. Chromatography in one form or other is to be preferred because in general the resolution obtainable with chromatographic methods rises with the lowering of sample size, and mass spectrometry is capable of dealing with very small sample sizes, in some cases well below the detection limit of the normal colorimetric or fluorometric methods.

Chromatographic separation

It is not difficult to separate small quantities (micrograms) of complex organic compounds by paper chromatography. The area containing the spot of the unknown is eluted with an organic solvent, the solution is concentrated by evaporation, and the concentrate admitted directly to the mass spectrometer. It is unfortunate that this process is surprisingly variable: sometimes the resulting mass spectrum can be matched very well with that of a standard, at other times the solvent may extract from the paper not only the sample material but also a great deal of contamination from the paper itself. The amount and nature of this contamination are dependent not only on the nature of the paper but also on its previous history, *i.e.*, which solvents it has already been exposed to during the chromatographic separation. Some improvements are observed when paper chromatography is replaced by thin-layer chromatography, on silica gel, cellulose *etc.* It has been possible, for example, to separate drugs from whole blood by a single separation upon cellulose and to identify the drug by removing a small area of the thin layer with a spatula and extracting with the appropriate eluent, filtering the slurry, evaporating the solvent and transferring the residue to the ion source in the manner described in the experimental section. Further, in the case of some compounds it has been possible to show that this process may be quantitative, so that submicrogram quantities of the components of complex mixtures may be separately identified and determined.[1]

When the sample components are sufficiently volatile they may be separated by gas chromatography. The very high efficiencies of separation obtainable with these methods, which greatly exceed those possible with fractionating columns, and their ability to deal with very small sample sizes, have encouraged experimenters to combine them with mass spectrometry. The separation of a pair of compounds by gas–liquid chromatography depends not only upon differences in the volatility of the two components but also upon differences in their interaction with the involatile liquid into which they are partitioned from the gas phase. As a result it is possible to take advantage not only of simple solution forces but of specific chemical interactions. It is thus possible, for example, to separate the *cis* and *trans* isomers of many simple hydrocarbons by using an involatile liquid containing a silver salt with which the unsaturated compounds form transient complexes. In a similar fashion the isomers of aromatic hydrocarbons may be separated by including in the involatile liquid some polynitro compound capable of forming molecular complexes with the aromatic. In each case some small difference in the stability of these complexes is exploited and quite small quantities of the involatile liquid are required. On the other hand, separations involving conventional solution forces may be made possible by having a very much larger quantity of the involatile liquid, maintained as a very thin film, and considerably multiplying the number of equilibrations of the sample mixture with the liquid. The limit to this is set only by purely experimental considerations of size and carrier gas inlet pressure. However, by an appropriate choice of column length and involatile liquid composition, it is possible to separate the components of complex mixtures of chemically very similar compounds. As an example, with the most efficient columns (either glass capillaries lined with squalane, or narrow packed columns with the same material dispersed upon small mesh size inert support) it is possible to separate deuterated hydrocarbons from their protonated counterparts. Dodecadeuterocyclohexane may be separated from normal cyclohexane with a relatively inefficient column of about 2000 theoretical plates, hexadeuterobenzene is separated from benzene, and trideuterotoluene from toluene[2] with packed or capillary columns with an efficiency of 10,000–15,000 plates, and with the highest efficiency columns of above 100,000 plates, monodeuterobenzene can be separated from benzene. The success of separations has in the past been limited by the inability of the gas chromatographic technique to provide an unequivocal means of identifying the separated species. The idea of specific retention volumes as a unique physical property which could be used for identification purposes has not been enthusiastically accepted by gas chromatographers. The determination of this constant, which is independent of temperature, gas flow-rate, involatile liquid concentration and sample size, required such precisely defined operating conditions that it was seldom used. A more successful compromise was the relative retention volume in which the retention volume of the unknown was expressed as a fraction of that of some similar known substance. Some variations in the experimental parameters were rendered less important but the uncertainties remained. Uncertainty could be removed by segregating the components of the mixture as they emerged from the chromatographic column, by adsorption on silica gel or alumina or by the passage of the effluent through a trap cooled in liquid air. A separate adsorbent tube or liquid-air trap was required for each component of the mixture requiring identification. The sample components recovered in this way were then identified by a second technique. Such a two-stage separation and identification does, however, involve difficulties, mainly resulting from the problem of manipulating small amounts of volatile material. This has resulted in the development of a direct coupling of the effluent from the gas chromatograph to the inlet system of the mass spectrometer, so that there is no handling process after the injection of the sample mixture into the inlet of the gas chromatograph. The manner in which this has been achieved is discussed in the section dealing with instrumentation and it is only necessary to point out that the problem of matching unknown and standard spectra is considerably simplified when the purity of the specimen is so assured. Further, although the retention volume is not normally determined with sufficient precision to make it a primary means of identification, it provides a useful additional piece of evidence to back up the mass spectra identification.

In all the foregoing it has been assumed that there exists a library spectrum of the unknown, and the only problem is that of matching. While this may be the case for some experimentalists, even in a routine analytical laboratory there will be times when the analyst will be faced with the identification of a completely new compound from its mass spectrum.

As outlined earlier, the mass spectrum presents a record of the unimolecular decomposition of an assembly of highly excited molecular ions. The chemistry of the decomposition is unique, and no great reward is obtained by comparisons with ground state chemistry or with radiolysis. And yet the only structural information available from a mass spectrum is that which can be gleaned from an understanding of the way in which the molecule ion breaks down. There are three distinct approaches to the problem of extracting this information. The analyst may attempt to understand this novel type of chemistry so that he may deduce the structure of the molecule ion from recognized decomposition processes. This approach is analogous to that by which many natural products were identified by classical organic chemical degradations, *e.g.*, pyrolysis or dehydrogenation. The second approach is to change the ionization process so that a different dissociation route is traversed. The third approach, which will commend itself most readily to the analytical chemist since he may make use of much of his armoury of chemical identification methods, is to modify the sample itself by means of a known chemical reaction and to infer the structure from a comparison of the mass spectrum before and after the chemical process. This method is analogous to the preparation of a derivative with a known physical property such as a melting point, absorption spectrum, R_f value or cryoscopic molecular weight. Our present understanding of the chemistry of the decomposition of ions has in fact been largely accumulated by studies involving the second and third approaches, and Beynon[3] in this country and McLafferty[4] in the United States have been particularly successful in expanding our understanding of the mechanisms involved. While it has been stressed that the chemistry of ion decomposition cannot be interpreted with the aid of an understanding of ground state mechanisms alone, there are certain features or underlying principles of chemical theory which must apply with equal force to these very fast reactions. It would be expected that the effect of neighbouring groups upon each other would be reflected in the rates of decomposition. An extreme example of this would be the so-called "*ortho* effect" where much stronger interactions would be expected between groups when they are adjacent to each other as substituents on a benzene ring than when they are more remote. Such an effect is observed and the spectra of isomers such as those of the nitrophenols or the hydroxybenzaldehydes are appreciably different (Fig. 1).

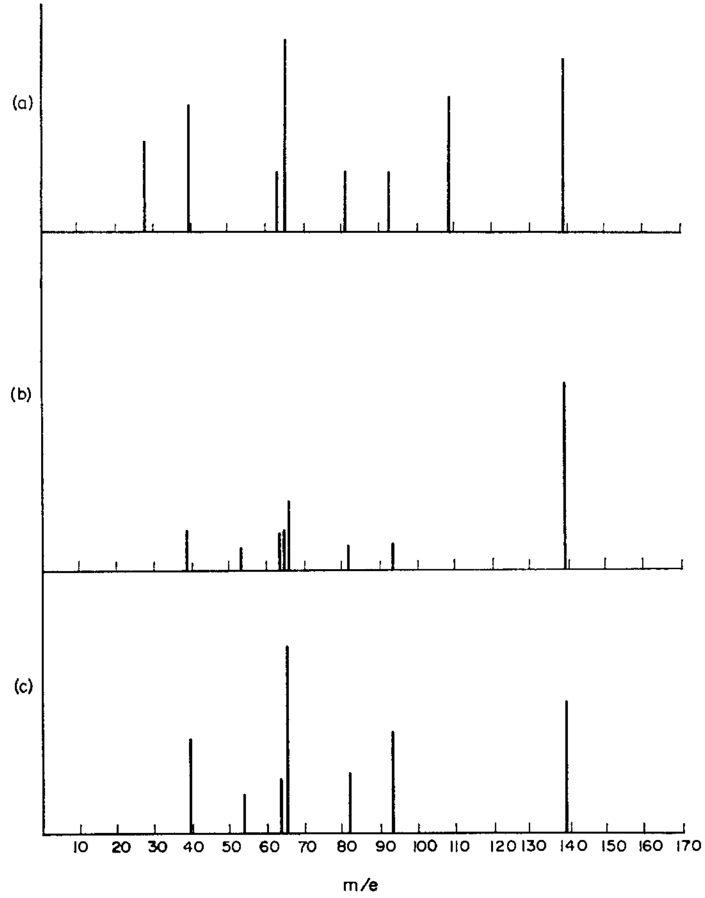


FIG. 1.—Mass spectra of nitrophenols: *a*, *p*-nitrophenol; *b*, *o*-nitrophenol; *c*, *m*-nitrophenol.

Since the energy is lost from the excited ion by breaking chemical bonds the strength of these bonds must have an effect upon the rate. As a result the rate of production of an ion from the molecule ion by the fission of a carbon–bromine bond would be expected to be much faster than if the same ion were being produced by the fission of a carbon–hydrogen bond, which has twice the bond dissociation energy. There are many examples in which this may be clearly demonstrated. The nature of the second species must also play a part in determining the rate of decomposition. Where the un-ionized fragment is a stable radical such as benzyl or allyl, then this dissociation is favoured. A very common example of the effect of the second species is when that species has a high electron affinity and so may readily form a negative ion with the release of up to 3 eV of energy. The most commonly observed example is the production of ion-pairs when compounds containing fluorine atoms are ionized. The high electron affinity of the fluorine atom results in the rapid dissociation of the molecule ion, and the mass spectra of most saturated fluorocarbons have negligibly small molecule ion peaks.[5] The most valuable information from a fundamental point of view would be the thermodynamic heats of formation of the ions, but although many values are available the thermochemical relationships have only been constructed for the simplest cases, and the main obstacle to their use in more complex systems is the lack of information about the excited states of the ions involved. If the mass spectrum represented only the results of the bond-breaking processes then the interpretation of most spectra would be greatly simplified. However, there are in addition a number of other processes occurring, leading to the formation of ions which could not arise by simple bond-breaking. The peaks in the mass spectra corresponding to ions produced in these processes were originally considered as noise, but recent improvements in instrumentation have provided more information about them and their recognition may actually aid structural analysis. These processes, which are normally called rearrangements, usually occur at low energies and result in the formation of an even-electron neutral species and an odd-electron ion, (*cf.* the bond-breaking process leads to the formation of an even-electron radical ion and an odd-electron atom or radical). An exception to this is when hydrogen atoms are involved. Hydrogen atoms appear to be quite mobile in the excited ion molecule and substantial rearrangements occur. Thus in the spectrum of 1,1,1-trideuterodimethyl sulphide[2] there are substantial peaks corresponding to the ions CD_2H^+ and CDH_2^+.[6] Another example of the mobility of atoms is the transfer to metal observed in the mass spectra of metal chelates. The spectrum of the titanium derivative of the diketone benzoyltrifluoroacetone exhibits peaks corresponding to ions in which one or two fluorine atoms have been transferred to the metal atom (Fig. 2). The elimination reactions referred to previously however may be more useful once they are understood. Certainly the most widely known of these rearrangement processes is the McLafferty rearrangement[7] in which the hydrogen atom gamma to a carbonyl or other electronegative group is transferred to the heteroatom with beta-cleavage of the molecular

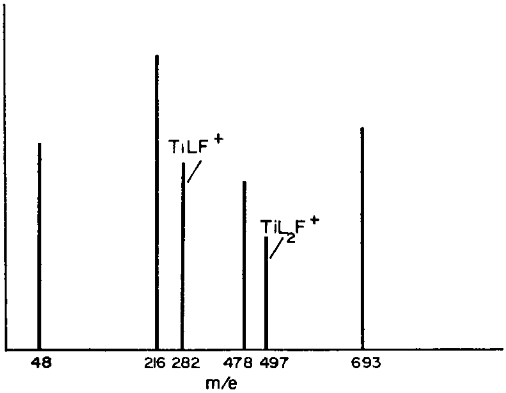


FIG. 2.—Mass spectrum of titanium benzoylacetonate, illustrating fluorine transfer to metal.

ion and the elimination of an unsaturated compound or a diradical (Fig. 3). Other examples include the elimination of CF_2 from atomatic compounds containing a CF_3 group, such as benzotrifluoride,[8] or the elimination of CO from aromatic ketones such as anthraquinone.[9]

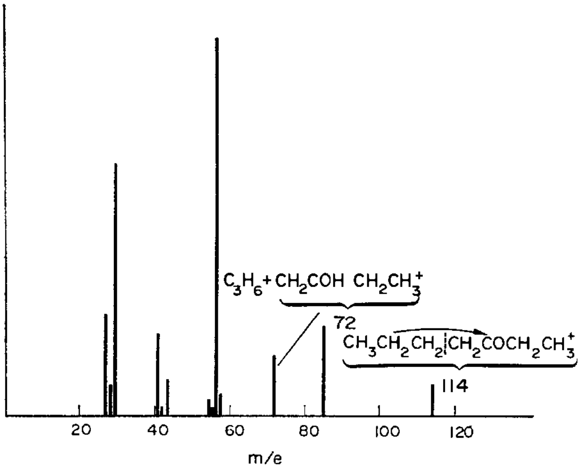


FIG. 3.—Mass spectrum of heptanone-3, illustrating the McLafferty rearrangement.

All these rearrangements lead to the formation of ions having an even mass (provided they do not contain an odd number of nitrogen atoms) and even-mass peaks other than molecule ion peaks are comparatively rare, so that it is easy to pick out the peaks due to rearrangement processes and to infer the structures from which they are formed.

In carrying out identification of unknown species by their mass spectrum alone, there are two techniques now available as a result of modern instrumentation, which are of the greatest assistance. The first of these is precise mass analysis which has been made possible by the development of high resolution instruments. The presently accepted mass scale uses carbon 12 as its standard, assigning it a mass of 12.000000. On this scale the mass of the hydrogen atom is 1.007825 while that of the oxygen atom is 15.994914. It follows that there is an appreciable difference in mass between ions having the same integral mass. Thus both carbon dioxide and propane ions have an integral mass of 44 but their precise masses of 43.989828 and 44.062600 differ by about 1 in 600. As a result a mass spectrometer with a resolution of 1000 can resolve the beams of carbon dioxide and propane ions when they are produced simultaneously and from the mass scale it is possible to say which is which. A higher resolution is required to resolve the mass doublet due to carbon monoxide and nitrogen molecule ions. It can be seen that an assembly of carbon, hydrogen and oxygen atoms gives a unique precise mass and this is true for any other atomic assembly. At the time of writing commerical mass spectrometers are available which have a mass resolution of 100,000 and masses of ions can be measured with a precision of 1 ppm. As a result it is possible to determine the atomic constitution of ions with a high degree of certainty. Taking, for example, the molecule ion of adrenaline, its precise mass is 183.089541 and the nearest precise mass to this which can be envisaged is 183.088195 which differs by one part in 180,000, which is considerably greater than the uncertainty of measurement. The atomic constitution is thus unequivocally determined as $C_9H_{13}O_3N$. The identification of the atomic composition from the precise mass can be carried out by the use of tables of the precise masses of atomic assemblies or may be done automatically with quite a simple computer programme. The atomic constitution of all ions represented in a mass spectrum can be identified provided that either the time or the instrumentation is available. It should be stressed, however, that despite the very great advance in understanding that such information provides, there is still at this stage no direct evidence as to the manner in which the atoms are linked together in the ions. It would be considered a reasonable assumption, on finding that peaks of mass 91 and 77 in the spectra of aromatic compounds were due to the atomic species $C_7H_7^+$ and $C_6H_5^+$, that these were in fact the benzyl and phenyl ions. There is evidence to the contrary, mainly arising from labelling studies, that these are seven membered ring and open-chain structures, respectively. Quantitative evidence about the structure of ions is scanty but there is good reason for believing that the doubly-charged ion of benzene no longer retains its cyclic structure.

The second technique which has been found useful in the study of ionic decomposition is that of metastable defocusing. It was pointed out in the earlier paragraphs that the reactions of ionic decomposition were extremely rapid and that the result of this was the consistency of the cracking pattern. In fact most of the chemistry is complete before the ion has left the source region of the instrument and proceeded to the analysis region, this journey taking a time of the order of a μsec. Some molecules in the ion source have relatively inefficient encounters with the ionizing electrons and as a result have lower amounts of excitation energy in the ions produced. The rate of dissociation of such ions is slower and weakly excited ions may escape from the source region of the instrument before undergoing reaction. The experimental result of this situation is that the ion, having acquired a velocity appropriate to its mass from the accelerating voltage gradient in the instrument, now changes its mass by the loss of a neutral fragment before being subjected to mass analysis. The magnetic field therefore brings this ion to a focus on the mass scale at a position which is neither the focus of the parent or the daughter ion but lower than either. In many cases the masses of the ions are related by the simple equation.

$$m^* = m_2^2/m_1$$

where m_1 is the parent mass, m_2 the daughter mass and m^* the apparent or metastable mass. The ions so produced have been erroneously named metastable ions and the peaks metastable peaks. These peaks may easily be identified in a mass spectrum by their appearance. They are most commonly very much wider than the normal peaks. This is due to the fact that the ionic decomposition is usually associated with the release of kinetic energy, which effectively increases the energy spread of the ion beam for that species only, and hence decreases the resolution, giving wider peaks. In fact there is a quantitative relationship between peak width and kinetic energy release and there have been a number of studies on this relationship, but of more general use is the facility of identifying the parent and daughter ion responsible for the metastable peak. Since the mass of each of these ions must be greater than that of the metastable peak position on the mass scale, and because there is normally a large ion current due to the parent ion, it is a fairly simple matter to find values of m_1 and m_2 which satisfy the equation. As an example, the mass spectra of most saturated hydrocarbons exhibit a peak at $m/e = 39{\cdot}1$ and the appropriate values of m_1 and m_2 for this metastable mass are 43 and 41 respectively. This means that the mode of decomposition can be identified, and on combining this technique with precise mass measurement it can be shown that the decomposition pathway is

$$C_3H_7^+ \rightarrow C_3H_5^+ + H_2$$

This of course does not imply that the $C_3H_7^+$ ion is either a propyl or an isopropyl ion; in fact, what evidence there is, arising from labelling studies, suggests a cyclic structure. In general, metastable peaks are less intense than those produced conventionally and the technique of metastable defocusing allows the operator to overcome this sensitivity problem and eliminate the difficulty of disentangling the normal and metastable spectra. The instrument is so adjusted that only those ions which have suffered a change in velocity as a result of a dissociation process taking place outside the ion source are able to pass a diaphragm situated after the energy selector of a double focusing instrument. The ion current due to ions formed within the ion source is not detected and the spectrum consists only of a series of metastable peaks, the intensity of which can be increased by increasing the amplification of the instrument, without at the same time increasing the signal due to the normal ion processes.[10] It is also possible to scan the spectrum in such a way as to identify all those decompositions associated with one particular ion.

The second approach in the identification of unknown compounds from their mass spectra is to gain additional information by varying the ionization process. The simplest way in which this may be achieved is to vary the energy in the ionizing electron beam. Many of the processes which are possible at energies of 70 eV cannot take place if the electron voltage is reduced to say 10 eV (see *e.g.*, Fig. 4). In some cases it may be possible to eliminate all the dissociation processes and obtain a spectrum which represents only the molecule ions of the sample components. This is however, easiest to achieve if the normal mass spectrum reveals a large molecule ion peak. Reducing the electron energy does not increase the total molecule ion current and may substantially reduce it, but it does increase the relative importance of the parent peak. An alternative to the reduction of electron energy is the substitution of the electron impact source by what has been called the field ionization source. If a molecule is exposed to a potential gradient which is similar to that existing at the outer electronic shells of the molecule then the outer low-energy electrons can escape and the molecule becomes ionized without the transfer of large amounts of excitation energy to the ion. A value of 10^8 V/cm is sufficient for this purpose and this can be created experimentally by a voltage of 10^5 V applied upon a sharp edge with a radius of a few hundred Å, such as a razor blade. The ions accelerated away from this edge are not highly excited and it is possible to create ions from molecules having weak chemical bonds, such as hydrates. Such species would not survive ionization by an electron impact source. Thus the spectrum produced by a field ionization source is very much simpler than that obtained with a conventional electron impact source and it is very much easier to identify the molecule ion.[11]

A further way in which ionization can take place has been studied by Field and relies upon ion–molecule interactions.[12] A conventional ion source is normally

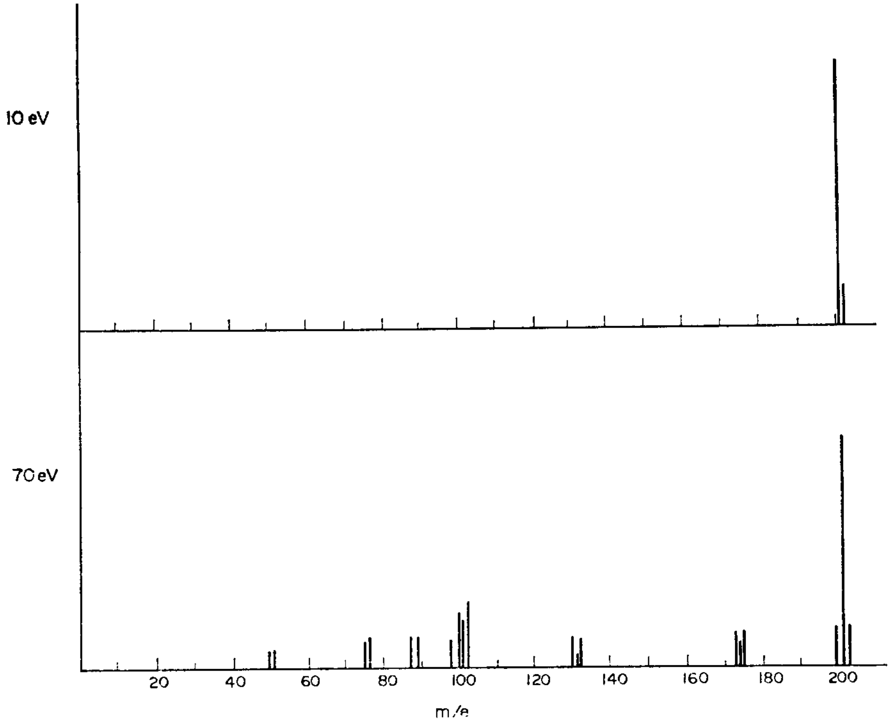


FIG. 4.—Mass spectrum of fluoranthene at 70 and 10 eV.

operated at a very low pressure so that the molecules have a long mean free path and secondary reactions are rendered insignificant. If, however, the pressure is allowed to rise above about 10^{-5} mm Hg the ion may interact with un-ionized gas molecules before it leaves the ion source. It has now become possible to eliminate the danger of producing gas discharges caused by the earthing of ion-accelerating voltages through a high pressure gas and to operate ion sources safely at pressures up to 1 mm Hg. If methane is ionized in such a source, then the methane ion, which is the initial result of the electron impact, abstracts a hydrogen atom from the methane gas to form CH_5^+.

$$CH_4 + CH_4^+ \rightarrow CH_5^+ + CH_3$$

If now a trace of a substance having a higher proton affinity is added to the methane, the proton is transferred to this molecule. The protonated molecule then decomposes in such a way that the charge remains with the fragment radicals. In this way an assembly of molecules gives rise to a mass spectrum with a different cracking pattern from that obtained by normal electron impact.

Finally, there is the purely chemical approach in which the sample substance is subjected to known reactions, the results of which are assessed by running additional mass spectra. The reactions chosen should be those which occur at room temperature (if possible) and lead to the formation of a derivative having a higher molecular weight than the original sample substance. There are a number of such reactions described in the literature, for the quantitative analysis of small amounts of compounds containing functional groups. The simplest possible reaction is that of deuteration. The sample is merely mixed with heavy water and allowed to equilibrate. Any labile hydrogen atoms such as those attached to oxygen atoms in hydroxyl or carboxyl groups will be replaced by deuterium. The result is that the mass spectrum, while retaining its overall pattern, will move to higher *m/e* values for those peaks which correspond to ions which have suffered deuteration. It is thus an easy matter to determine the number of hydrogen atoms replaced and which therefore were attached to oxygen. A second specific reaction which may be used with advantage is the conversion of aldehydes into aldoximes with hydroxylamine hydrochloride solution. For each aldehyde group converted the spectrum moves 15 mass units. The simplicity of this approach is that these reactions may be carried out on the microgram scale on the probe of the mass spectrometer, and the reaction products analysed without any pretreatment. As an example, the following three spectra (Fig. 5) show the spectrum of an alkaloid precursor[13] and its reaction products with heavy water and hydroxylamine hydrochloride. The presence of one hydroxyl and one aldehyde group is clearly indicated and the structure of the compound has been shown to be

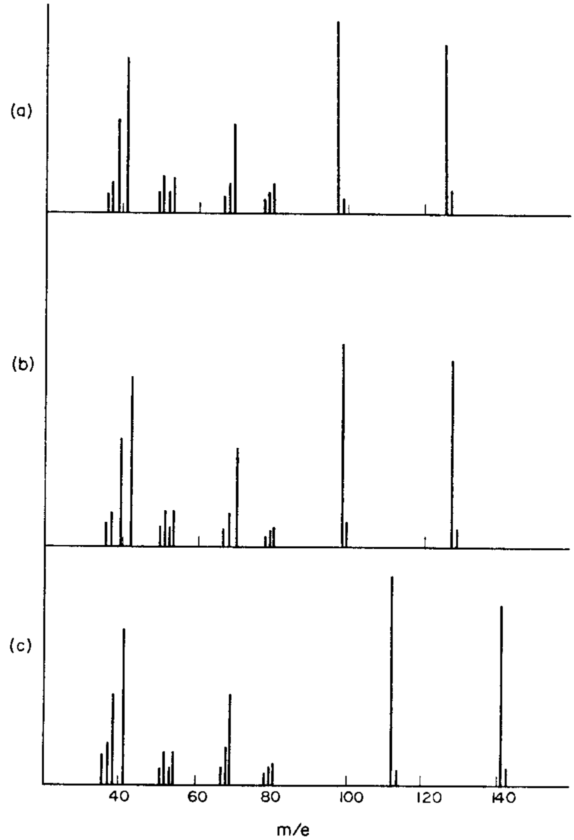
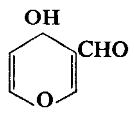


FIG. 5.—Determination of structure by the formation of derivatives: *a*, hydroxypyrone aldehyde; *b*, after deuteration; *c*, after forming the oxime.



INSTRUMENTATION

Mass spectrometry shares with the technique of molecular beams the distinction of being the physical method slowest to receive widespread acceptance and exploitation by the chemist. Both were being used by the physicist before the last war and it is only recently that the mass spectrometer has taken its place beside optical spectrometers in the laboratory for routine sampling and analysis. In no other technique has there been such widespread proliferation of instrumentation or so wide an application to diverse analytical problems. In this section the main types of instrument will be discussed and examples given. A more complete review has been made by Beynon and Fontaine.[14]

At the present time, because of the very diverse nature of the instruments which may be classed as mass spectrometers, it is necessary to define the instrument in the most general terms. The one feature which all instruments have in common is that ionization and mass analysis take place in a high vacuum system. Briefly then, a mass spectrometer is a device which is capable of introducing a sample into a high vacuum and converting a proportion of the molecules in the resulting vapour into ions. The ions so produced are classified according to their mass to charge ratio (m/e) and the abundances of each ionic species is measured and recorded. As will be discussed in a later section, because such measurement and recording takes an appreciable interval of time, ion abundances must be detected as ion currents n_1/t. In order to give any significance to such ion currents, it is necessary to maintain a constant partial pressure n_{M} of the sample in the source and to keep a constant rate of ionization n_X/t. These considerations are unimportant in the design of a mass spectrograph, where only the masses of the individual ions are to be measured. These instruments, however, are comparatively rare.

The story of the development of the modern mass spectrometer is an account of continued efforts to improve the sensitivity of the machine, to increase its ability to distinguish between ions of closely similar mass, *i.e.*, its mass resolution ($m/\Delta m$) and to decrease the time taken to record the magnitude of the ion currents, *i.e.*, the mass spectrum. At the same time there have been attempts to increase the range of the instrument both in the production of ions of higher m/e values and in the classification and recording of such ion currents.

180°-*Focusing instruments*

An ion moving with uniform velocity in a magnetic field at right angles to the plane of its motion describes a circular path provided that the magnetic field is constant and uniform. This principle was exploited in the earliest form of mass spectrometer described by Dempster[15] in 1918, and it is of considerable interest that an instrument of this type is still in an active stage of development today. Positive ions are accelerated in a potential gradient V and enter a uniform magnetic field H which is perpendicular to the direction of their motion. The ions of mass m aquire a velocity v and so have an energy given by $\frac{1}{2}mv^2 = \mathrm{e}\mathrm{V}$, where e is the electronic charge. The radius R of the circular path which the ions describe is then given by the equation

$$Hev = \frac{mv^2}{R}$$

On combination of these two equations the field and potential gradient requirements for an ion with mass to charge ratio m/e travelling in an orbit of radius R are given by

$$m/e = \frac{H^2R^2}{2V}$$

The uniform magnetic field has a focusing action equivalent to that of a cylindrical lens so that beams of ions issuing from a slit are brought to a focus after suffering a deflection of 180° to form a first-order image of the slit with ions of the appropriate m/e values for the given field strength and potential gradient. This system is thus direction-focusing so that it is not necessary to inject a parallel beam of ions into the magnetic field. On the other hand, it requires that all ions having the same m/e value should have the same velocity v, that is to say this is not an energy-focusing system. The resolution of this type of instrument depends upon the homogeneity of the magnetic field over the whole of the ion path, the stability of the ion-accelerating potential difference and the width of the entrance and exit slits. The optimum values for slitwidths are those in which a successful compromise is achieved between the increase in resolution obtained by reducing slitwidth and the accompanying reduction in sensitivity.

Before giving any actual values of mass resolution achieved by various instruments, it is necessary to make a satisfactory definition of the term $m/\Delta m$. The original definition used by Dempster is expressed in the formula

$$m/\Delta m = R/(S_1 + S_2)$$

where S_1 and S_2 are the entrance and exit slitwidths. This makes the assumption that a perfect image of the entrance slits is formed in the plane of the exit slit and that the adjacent beams of ions are resolved when one image occupies the exit slit while none of the ion current due to the adjacent image enters the exit slit. Owing to imperfections of the experimentally attainable ion optics system, this simple equation cannot be retained as an adequate definition of mass resolution. The image will be distorted, having chromatic aberration due to variations in the kinetic energy of ions of the same mass and would have "wings" on either side due to the gas scattering in the ion path. These aberrations are taken into account by assuming a constant β such that the effect of the aberrations is shown to be proportional to the radius of curvature of the ion path as in

$$m/\Delta m = R/(S_1 + S_2 + \beta R)$$

Despite the obvious value of this equation it is more common to apply an empirical definition of mass resolution in which unit resolution is said to be achieved when there is a valley between adjacent peaks in a mass spectrum record. The peaks should be of equal height and the depth of the valley is chosen arbitrarily; the height of the valley above the base-line is expressed as a fraction of the peak height. When comparing the advertised performance of commercial instruments or the published figures for mass resolution of experimental instruments, it is important to identify the criterion which has been applied for unit mass resolution, as this can range over two orders of magnitude. Alternative criteria for resolution which have been suggested are based on peak width or contribution to a mass peak from an adjacent peak of the same height. The effect of slitwidth on mass resolution in a modern 180°-focusing mass spectrometer is illustrated in Fig. 6 which shows a mass spectrum for krypton recorded with slitwidths of 0·25 and 0·50 mm.

The stability and simplicity of this method of mass selection has led to its adoption and development in a range of low-resolution instruments. In particular, Associated Electrical Industries have produced a number of commercial instruments under the generic name of M.S. 10 and 20, based on a design with a radius (*R*) of 5 cm. These instruments are still in a state of active development and improvement. The original design used a large permanent magnet with a field strength (*H*) of 1840 gauss. Scanning of a mass range of 1–200 was achieved by varying the accelerating voltage (*V*) either continuously or in steps. The resolution which could be achieved with a slitwidth of 0·50 mm was 40 with a 2% peak valley between adjacent peaks of equal height. This type of instrument is suitable for use as a sophisticated ionization gauge, when it may be bolted directly to the vacuum system being monitored. Alternatively, it may be used for leak testing, by using a gas with a characteristic mass spectrum as the test gas for tracing the leak in a vacuum system. The resolution is adequate for the identification of most of the residual gases found in high-vacuum systems.

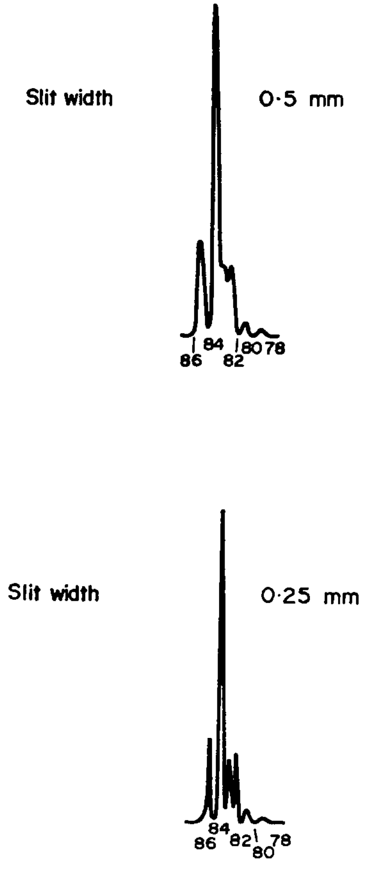


Fig. 6.—Effect of slitwidth on resolution: mass spectrum of krypton.

Recently, this design has been modified so as to convert the instrument into a versatile mass spectrometer for low-resolution general analytical studies. The mass range has been extended to 1000 by replacing the permanent magnet with a large electromagnet capable of providing fields up to 11,000 gauss. The resolution has been increased to approximately 550 by reducing the slitwidths to 0·025 mm and increasing the detector sensitivity. This design is particularly flexible since it permits the magnetic field to be swept at a number of alternative accelerating potentials.

The same company also produced a greatly simplified design in the Minimass Partial Pressure Gauge. The radius has been reduced to 1 cm and a small permanent magnet with a field strength of 4000 gauss is employed. Voltage scanning up to mass 240 permits the identification of each mass on a linear scale and the mass resolution is approximately 28 with 50% peak valley between adjacent peaks. This inexpensive compact model is intended for monitoring vacuum systems.

Similar models to the M.S. 10 range have been produced by the Atlas Co.* of Germany ($R = 28$ mm, $H = 2750$–4000 gauss, $m/\Delta m$ 18–44) and the Consolidated Electrodynamics Corporation of the U.S.A. ($H = 800$–6000 gauss, $m/\Delta m$ up to 600 with an electrostatic slit).

The chief advantage of the 180°-focusing system has been its comparative simplicity and consequent low price. The chief disadvantage in the past has been the necessity to scan the mass range by adjusting the ion-accelerating potential (V) so that ions are collected with varying efficiencies, the heavier ions requiring low potentials. Thus the sensitivity is lowest for ions with the highest m/e value and since in general such ion currents will give the most information from an analytical point of view, this reduction in sensitivity is a disadvantage. The recent substitution of large pole-face area electromagnets for the conventional permanent magnet has eliminated this disadvantage, permitting magnetic scanning. Although there is a corresponding rise in cost, the resulting flexibility has made this type of instrument the most important of the low-resolution magnetic series. The limiting factors in any further improvement of performance with this type of machine are the mechanical difficulties associated with providing source slitwidths of less than 0·025 mm and the resulting problem of providing additional detector sensitivity.

Sector field instruments

It was shown in 1940 that the phenomenon of the focusing of ion beams by causing deflection through 180° in a homogeneous magnetic field was in fact a special case of focusing by means of an inhomogenous field.[16] The ion beam should leave and enter the magnetic field at right angles to the field boundary and inside the field the ion describes a path which is a sector of a circle. The angle subtended by this sector may be 60°, 90° or in the limiting case above, 180°. The separation of ions of different mass to charge ratios takes place in an exactly analogous manner and beams of ions from the source situated some distance from the field boundary are brought to a focus at a collector symmetrically disposed on the other side of the sector magnetic field. The disadvantages of this type of geometry are the long path with consequent greater probability of collisional scattering, and the difficulties associated with the precise alignment of the sector magnetic field to obtain satisfactory focusing. On the other hand, there are considerable advantages in having both source and collector in

---

* Now Varian Mat.

field-free regions. The source is more readily accessible so that a variety of modifications may be carried out and the collector may be fitted without difficulty with an electron multiplier to increase detector sensitivity.

The most successful machine of this type was first introduced by the Metropolitan-Vickers Company (now G.E.C./A.E.I.) just before 1950. The M.S. 2 was a 90°-sector 15-cm radius instrument issued originally with a mechanically adjustable collector slit providing a maximum resolution of about 300. This resolution was later doubled by the use of a collector slit having an effective width which could be altered by giving it a high positive potential. For quantitative studies the collector slit was set at 0·62 mm to give a lower resolution but increased reproducibility, the record being in the form of a series of flat-topped rather than pointed mass peaks. A greatly improved version using the same basic geometry with a 90° sector of radius 15 cm was the M.S. 2H. The addition of an electron multiplier at the collector provided increased sensitivity, permitting a further increase in resolution to above 650. The mass range with the normal accelerating voltage of 2 kV was extended to 650 by increasing the magnetic field.

There have been a number of variations on this type of instrument, the most notable being the Atlas CH_4 with a resolution in excess of 1000.

A further stage in the improvement of the performance of the 90°-sector field instrument was provided by the A.E.I. M.S. 12 design in which the radius of curvature had been increased to 30 cm. A further decrease in slitwidth to 0·0125 mm was made possible by increasing the ion accelerating potential to 8 kV and with an electron multiplier detector a mass resolution of 7500 was achieved. In this design, which is now obsolete, both magnetic and voltage scanning facilities were provided, the latter permitting a mass spectrum to be displayed in less than 1/5 sec.

Double-focusing instruments

A beam of positive ions may also be analysed according to the velocity which the ions have attained. This velocity is proportional to the square root of the mass, provided that all the ions have suffered the same acceleration in a potential gradient, and velocity analysis is normally achieved by passage through transverse electrostatic fields. The principle of combining velocity and mass analysis to provide instruments having both direction and velocity focusing of beams of ions was discussed by a number of mass spectrometrists but little progress was made until Mattauch and Herzog[17] formulated their theory of double focusing, employing a radial electrostatic field for which $R\,dV/dR =$ constant where R is the radius and V the potential, and there is a homogeneous sector magnetic field. The improvements in the definition of the ion optic image made possible by the application of this principle stimulated the construction of a number of double-focusing instruments, culminating in the commercial development of two different types.

The first of these commercial double-focusing mass spectrometers was described in 1958 by Craig and Errock.[18] It was based upon the geometry suggested by Nier and Johnson[19] and was marketed as the first instrument specifically designed for the qualitative analysis of organic compounds. The commercial version became the A.E.I. M.S. 9 mass spectrometer.* It combined a magnetic sector of 90° with a radius

---

* Similar instruments have been developed by the Hitachi Organization in Japan and marketed by Perkin–Elmer.

of 15 cm, with an electrostatic analyser of radius 18·25 cm. A source slitwidth of 6·25 μm was used to give a resolution of 10,000. The instrument had the novel features of oscilloscope peak-matching, by which the precise masses of known and unknown ions were compared, with an accuracy sufficient to permit the identification of the atomic constitution of the unknown ion provided it had a mass of about 200. A further feature was the ability to record the spectra of compounds of low volatility by direct sample insertion into the ion source. There has been a steady improvement in the performance of the double-focusing instrument over the past ten years and the most recent models have a magnetic sector of 30 cm radius and an electrostatic sector of 38 cm radius with a source slit that can be reduced to 0·1 μm to give a resolving power of 100,000. At lower resolving powers the scan duration can be reduced to 2 sec. Additional features have included combined electron bombardment, field emission and water-cooled sources to permit the study of labile organic compounds. With a spectrometer having these characteristics it is possible to determine the atomic constitution of almost all the ions normally responsible for the peaks in a mass spectrum. However, making a number of precise mass determinations by the peak comparison technique is time-consuming and the most recent development is to carry out these determinations automatically by the aid of a small computer. The output from the spectrometer is digitized and the centroid of each mass peak determined from a score of ion current measurements or by differentiation. The centroids of known and unknown peaks are then compared not in terms of accelerating voltage as in the manual technique, but in terms of time with the aid of a megacycle clock. The spectra may be stored on magnetic tape to be played back in analogue form or they may be printed out in the form of a table of atomic constitution and ion abundance.

Double-beam mass spectrometer

The most recent development in instrument design has been the production of a double-beam instrument by the A.E.I. organization (M.S. 30). The beams from two ion sources are bent so as to pass through a single mass-analyser system and then allowed to diverge to two separate detectors. With such an arrangement it is possible to compare the spectra of two compounds recorded at the same time on a single chart recorder. The spectra may be of known and unknown compounds, permitting direct chemical mass marking or matching of spectra. The two spectra may equally well be those of a single compound ionized and analysed under different conditions, e.g., high and low resolution or electron voltage. The operation of this instrument has been simplified so as to make it appeal to the routine analyst. The multiplicity of controls on older models has been replaced by a few interlocked push buttons.

Spark-source mass spectrography

In the double-focusing high-resolution mass spectrometers described above, the deflection due to the electrostatic and magnetic sectors is in the same sense. In an alternative geometry, ion optic image corrections and double focusing may also be achieved if the two deflections have opposite senses.[20] In addition to providing high resolution, this geometry has the further advantage that all ions are brought to a focus in one plane. The result is that a complete mass spectrum may be recorded simultaneously by placing a photographic plate in this plane. These features were exploited successfully in instruments produced by the A.E.I. company in this country and the Atlas Co. in Germany. The ability of the double focusing system to accommodate ions with a large spread of kinetic energy made it possible to use an instrument for elemental analysis in which the ionization was carried out with a high-frequency spark. In the A.E.I. M.S. 7 the substances to be submitted to elemental analysis were incorporated into carbon electrodes if they were themselves non-conducting and submitted to the action of a high-frequency spark in the ion source region. The resulting vapour was then ionized and the ions submitted to mass analysis. Detection was by means of a photographic plate which not only permitted the simultaneous recording of ion currents at all masses but also compensated for variations in spark intensity by integrating ion current with time. The final measurement of ion abundance was made by developing the plate and measuring the density of the appropriate line. Comparisons with standards permitted quantitation of the technique and made it a competitor to emission spectrography. The great advantage of spark-source mass spectrometry is its ability to give a quantitative analysis of a large number of trace elements at the same time with only a few exposures. The limit of detection is very much lower than that of any other technique except activation analysis. Limits of detection of 1 in 10^9 are frequently quoted and the sample size may be as small as 50 mg.

While this type of instrument is eminently suitable for photoplate detection, the plate can be replaced by a slit and the ion current detected electrically. The spectrum may be scanned past the slit as in other instruments. This versatility has been made use of in designs developed by the Atlas company, who have marketed models which can be used with either electron bombardment or spark sources and with either photographic or electrical detection.

Mass filters

There are three types of non-magnetic mass analysers which can be classed as mass filters, that is devices in which radiofrequency fields are used to selectively exclude ions from a detector; they are classed according to their electrode systems and have been given the names of the quadrupole, the monopole and the three-electrode mass filters.

The quadrupole system consists of four rods which are mounted along the direction of the ion path between the ion source and the collector. The ions enter the space between the rods where they experience a radiofrequency field. Paul was the first to describe such an arrangement and in his design the rods were collinear and symmetrically disposed around the ion path, with opposite pairs being interconnected.[21] The potentials applied to the rods are as follows

$$V_x = U + V \cos \omega t$$

and

$$V_x = -V_y$$

where V is the amplitude of an RF sinewave of frequency ω, U is a superimposed d.c. voltage and x and y are planes at right angles to the ion path. Theoretically the rods should have a hyperbolic cross-section; in practice, with the exception of the instrument marketed by Industrial and Technical Equipment Co. Ltd., the cross-section is circular, and it is usual to make the distance between opposite pairs of rods smaller than the rod diameter by a factor of 1·16.

Under the conditions that $U/V < \frac{1}{6}$ for a given value of the RF amplitude V, only ions within a very small mass range can execute stable trajectories along the length of the rods and escape to the detector. All other ions have unstable trajectories which end in a collision with the rods. In order to scan a mass spectrum either the frequency or the RF amplitude V may be swept and for wide scans a combination has been preferred. Rods are about 20 cm long and 0·6 cm in diameter, so the assembly provides a very compact mass analyser. The upper frequency range is determined by power requirements and is about 5 MHz. The great advantage of this type of analyser is that it is insensitive to variations in ion energy, so quite crude sources can be used. On the other hand, it has the disadvantage of requiring very precise rod alignment and stability, of the order of a few thousandths of a centimeter. The power supplies must also be very stable and for the highest resolution the U/V ratio must be kept constant within at least 1 in 20,000. The first commercial mass filter was produced by the Atlas Co. in Germany in 1963. It has a resolution of 100 and a mass range of 2–100. More elaborate instruments have been produced by the E.A.I. Co. and most recently by the Finnegan Instrument Corporation. The latter organization has produced the mass filter with the highest performance, it being capable of scanning up to a mass of 750 with a resolution of 1000. Other instruments with more modest performances have been introduced by GEC/AEI, Vacuum Generators, Baltzers, 20th Century Electronics and Varian. The ability of the mass filter to scan a wide mass-range in a very short time interval has been exploited in the mass spectrometer/gas chromatograph combination described later. While in theory very high resolutions are accessible with the mass filter, at present it is in the stage of being an inexpensive low- and medium-resolution device having the virtue of rapid scan and small size.

The monopole

It was first pointed out by von Zahn that one quarter of the geometry of the quadrupole could be replaced by a single rod and a grounded electrode with a right angle cross-section.[22] The operation is the same, both RF and d.c. voltages being applied to the rod and scanning achieved by sweeping either the RF frequency or amplitude. As in the case of the quadrupole, the monopole suffers from the disadvantage of giving spiked peaks rather than the flat-topped peaks produced by magnetic sector instruments. On the other hand the monopole has the advantages of providing spatial separation of ions so that it is feasible to record several ion currents at the same time. In addition, the stability requirement of the U/V ratio is greatly reduced so that simple power supplies can be used while good resolution can be achieved without the same mechanical requirements. The chief disadvantage of the design is the sensitivity to contamination by particulate matter, which causes peak splitting, while small changes in the operating conditions may introduce large variations in the relative intensities of the ion currents. Nevertheless, a successful monopole partial pressure gauge *i.e.*, a low-resolution monopole, has been marketed by Veeco Instruments Ltd. It has a mass scan of 1–200, a resolution of 50 and a minimum detectable total pressure of 5×10^{-9} mm Hg.

The three-electrode analyser

This was first described by Fischer.[23] It is a very compact arrangement, each electrode being part of a hyperboloid of rotation. In practice this amounts to a ball-bearing being placed above and below a ring of the same cross-section. It will be at once realized that the quadrupole and three-electrode assemblies have the same cross-section geometries but the latter is in fact a three-dimensional device so that ions cannot escape from a field between the electrodes once they have entered it. The ions circulate continuously around the axis of the field, unstable ions being lost as before by collision with the electrodes. The stable ion current is detected by means of the inductive load which it presents to an external oscillator. High sensitivity has been obtained for the three-electrode system in experimental models, which have detected as few as 10,000 ions. There is also the possibility of storing ions for relatively long periods and hence integrating weak ion currents.

Time-of-flight mass spectrometers

In the time-of-flight mass spectrometer first described by Stevens[24] the ionizing electron beam was intermittent rather than continuous. The electron pulse lasted about 0·1 μsec and the time of a complete cycle was about 100 μsec. The ions formed during the pulse were accelerated into a drift tube which they traversed on their way to a detector. The rate of travel was inversely proportional to the square root of the mass to charge ratio, and with sufficiently good time resolution of the signal obtained from the detector it was possible to isolate the individual pulses produced by the separated bunches of ions. An oscilloscope was the most suitable means of displaying such a spectrum, provided that the time-base was coupled to the pulsing circuits. The original designs were rather insensitive but later instruments stored ions in the source for a few μsec before initiating the analysis, and commercial instruments such as that manufactured by the Bendix Co. have sensitivities which are comparable with those of other instruments. While repetition rates as high as 100,000 per sec at resolutions approaching 1000 are possible, it is important to stress the fact that the dynamic range under such conditions is low and good analytical operation is only possible by integration over some hundreds of cycles.

The great advantage of this type of mass analyser is the simplicity of the source and non-critical nature of the source and flight-tube geometry. Apart from the ability of the detector circuits to resolve smaller and smaller time intervals the only way of increasing the resolution of time-of-flight instruments is to increase the length of the path between source and collector. In order to prevent the size of the drift tube becoming unmanageably long the ions may be constrained by magnetic fields to move in a helix. A device of this type was recently described under the name of the Spiratron.[25] It is interesting that under these flight conditions the more energetic ions move in longer paths and arrive at the detector later, thus providing the possibility of a two-stage instrument. In this a helical path is coupled with a straight path in which the more energetic ions arrive first, thus eliminating the reduction in resolution caused by energy spread of the ion beam.

APPLICATIONS

Coupling with the gas chromatograph

The advantages of the direct coupling of the effluent of a gas chromatographic apparatus with the inlet system of a mass spectrometer were outlined in the introduction. The methods of carrying out the combination are discussed briefly here; for a more detailed discussion the reader is directed to earlier reviews.[26,27] There are two problems associated with such a combination, the first being the necessity of recording the mass spectrum during the period in which the sample is emerging from the base of the chromatographic column. This time may vary from about 10 sec to above 1 min, but during this time, in which the signal is rising and falling on the chromatograph detector, the concentration of the sample in the effluent carrier gas stream is rising and falling also. It is advantageous to record the mass spectrum with a constant sample pressure since otherwise the relative intensities of the ion currents will not be constant and the matching procedure referred to earlier will not be possible. For these reasons it is important to record the spectrum in a fraction of the time required for the whole of the sample to emerge and to make this record when the concentration is at its maximum. (Or alternatively to use a normalizing procedure based on a total ion-current measurement.) It is easier to change the accelerating voltage rapidly than to alter the magnetic field, and in many simple combination instruments the mass decade can be scanned in a second or less. Recent advances in instrumentation of magnetic instruments have made it possible to scan a mass decade magnetically in about 2 sec. This eliminates the disadvantage (associated with voltage scanning) of the lower efficiency of collection of the heavier ions. Much faster times of scanning are available with non-magnetic instruments and no problems are encountered with their use, for these reasons. A rapid scan allows the experimenter to examine partially resolved chromatographic peaks by recording the mass spectrum at the beginning and end of the chromatographic peak. In these spectra the role of the two sample components in the two spectra will be revealed.

The second problem associated with the direct coupling of the two instruments is the carrier gas. Even when the sample is at its highest concentration in the carrier gas effluent from the column, it is still present as only a small fraction of the carrier gas concentration. The direct admission of the carrier gas stream to the ion source would therefore result in the production of a high source pressure and in the recording of a mass spectrum which was largely that of the carrier gas itself. In order to overcome this problem it is necessary to achieve a segregation of the sample and to admit only it to the ion source, preferably without any loss of the sample. This ideal case has never been achieved in practice but there have been three successful compromises.

The first of these was developed by Ryhage and relied upon the effusion of the gas mixture from a narrow orifice for its separation.[28] The carrier gas used was helium and together with the sample the effluent passed through such a jet into a chamber at a reduced pressure. Immediately opposite to the jet was a small aperture leading to a second jet. The helium, because of its low gas density, had a high component of velocity at right angles to the line of flow and so collided with the chamber walls and was pumped away. The heavier sample molecules entered the aperture and issued together with a reduced amount of helium to the second jet where the process was repeated, the final aperture leading directly to the ion source and the second chamber being held at a pressure lower than that in the first chamber. Recoveries of the order of 50% of the original sample were achieved and the carrier gas concentration was reduced to 2%.

The second method also depended for its success on the exploitation of the low density of helium. The Watson-Biemann separator[29] allowed the effluent to pass into a tube made of glass frit or sinter. An outer jacket surrounded the frit and the annular space was continuously pumped out. The helium diffused through while the sample passed along the tube to the ion source. Recoveries of about 15% were achieved and the carrier gas concentration was reduced to a few per cent.

The third separator, which is now promising to oust all the others (although at present the majority use a glass frit separator) because of its cheapness and simplicity, was originally suggested by several investigators and is called the membrane separator. It uses a thin film of a polymer, usually silicone rubber, to divide the effluent stream from the ion source. The sample components are soluble in the membrane and diffuse through it into the ion source while the carrier gas is excluded. To eliminate memory effects and to increase the rate of diffusion and hence the response time, the film must be made as thin as possible. The recovery can be as high as 25% and the residual carrier gas concentration as low as 5%. All three separators are usually heated in order to increase the rate of the separation process and to reduce adsorption. There are a number of commercial instruments sold as a gas chromatograph–mass spectrometer package. The first successful design was the LKB 9000 which used the Ryhage separator, had a resolution of about 1000 and required a total sample size of only 0·1 μg. The GEC/AEI Co. used the glass frit separator in their M.S. 12 which in its final stages of development had a resolution of 7500 and required a sample size of only 2 μg. The M.S. 12 has now been replaced by the M.S. 30 double-beam instrument described previously, which uses a membrane separator. Lower resolution magnetic sector combinations have been developed by Edwards High Vacuum Ltd., and Vacuum Generators Ltd. The GEC/AEI Co. have combined their 180°-focusing instrument (the M.S. 20) with a gas chromatograph. The rapid-scan facility and low cost of the quadrupole mass filter have made it an attractive gas chromatograph detector and the EAI Co. and the Finnegan Instrument Co. in the U.S.A. have manufactured competitors to the magnetic instruments, using both frit and membrane separators. The resolution is in the 500–1000 range and the sensitivity is 3×10^{-11} g/sec. They have a very high scan-rate and indeed the scan-rate of all the instruments described is sufficiently fast to permit oscilloscope presentation of spectra. This is a useful facility because whether chromatographic peak detection is made by an external detector or by the ionization facilities of the instrument operating at an electron voltage below that of the ionization potential of the carrier gas, no peak identification is possible until the spectrum is run. The use of the oscilloscope obviates the need for the recording of unrequired mass spectra merely for peak identification purposes. In an analysis of a complex sample mixture this could be a costly undertaking.

The determination of isotopic constitution

The examination of any mass spectrum of an organic compound immediately reveals the polyisotopic nature of naturally occurring carbon, sulphur, chlorine, bromine and boron. The small proportions of the heavier stable isotopes of hydrogen, nitrogen and oxygen are less obvious. All these isotopes are stable and should not be confused with artificially produced radioactive isotopes such as carbon-14. The very great success of labelling techniques based on radioactive isotopes may be shared to some extent by the use of artificially enriched stable isotopes. The ability of the mass spectrometer to detect stable isotopes can never be as great as the ability of the counter to detect radioactive isotopes, but the great advantage is that the stable isotopes may be handled with none of the precautions inherent in the handling of radioactive compounds. The principles involved in tracing with stable isotopes are, however, exactly the same, the change in the isotopic constitution of samples (drawn from a dynamic or reacting system) being assayed by the mass spectrometer, and the signal at the abnormal isotope peak being analogous to the signal derived from the counter.

There is, however, a further advantage in the mass spectrometer method, because the ionization is followed by a dissociation process in which the labelling atoms are combined with fewer and fewer of the other atoms in the molecule. Thus an examination of the spectrum can give information not only on the extent of labelling but also on the position of labelling within the structure. In order to do this of course it may be necessary to use all the techniques which have already been outlined in previous paragraphs, such as precise mass determination.

If now the spectra of the labelled and unlabelled molecules are compared and the atomic constitution of the fragment ions is determined, it will be seen that the labelled atom is concentrated in one part of the molecule. This of course can only be achieved when the label atom is part of the backbone of the molecule. As has been observed earlier, hydrogen and deuterium atoms are notoriously labile in the ions and it is difficult to draw any but statistical conclusions from such labelling. This determination of the site of introduction of the label atom depends upon the ionization of a compound sufficiently volatile to permit evaporation into the source of the mass spectrometer. In some cases, because of the complexity of the reaction mixture or the intractable nature of the products, it may not be possible to make such a determination. It may still be feasible to get tracing information by conversion of the reaction mixture or some part of it into a volatile product which contains the stable isotope. In the case of carbon-14, radioactive tracing of the labelled compound is achieved by conversion into carbon dioxide or even methane. A similar conversion may be carried out with compounds containing carbon-13 and the ion current at $m/e = 45$ used as a measure of the total carbon-13 content. In a similar way the nitrogen-15 content of, for example, excreted urea, may be determined by Kjeldahl digestion followed by a hypobromite treatment to release molecular nitrogen. The ion current at $m/e = 29$ is a measure of the enrichment of the sample. Oxygen-18 may be assayed by pyrolysis followed by the oxidation of the carbon monoxide to carbon dioxide. The ^{18}O concentration is measured at $m/e = 46$. The precision of these measurements can be quite high and is improved by integrating the results of a number of measurements. The sensitivity depends upon the dynamic range of the instrument and can have a value of 0·01 atom %. When determinations of the isotopic concentration of both carbon and nitrogen are required the mass spectrometer may be connected directly to a conventional C, H, N analyser.

The very great advantage of the stable isotope method of tracing is that quite highly labelled material may be fed to experimental animals or patients without fear of the side-effects arising from the administration of similar doses of radioactive material. With the increasing availability of compounds labelled with ^{13}C, ^{15}N and ^{18}O and the wide distribution of moderately priced instruments capable of analysing them, a large increase may be expected in the use of stable isotope tracing in the biochemical and medical fields.

Quantitative analysis

With an ion source with a constant ionizing electron beam current and with a constant source pressure of the sample gas it is possible to determine the sensitivity of an instrument for any particular substance. Since in general any substance will produce ion currents at a number of different m/e values the sensitivity at any one of these values may be chosen. In the absence of any reason to the contrary the value chosen will be that at which the most intense ion current is produced, that is to say the m/e value corresponding to the highest peak in the mass spectrum. It is however difficult to record the pressure of the sample vapour in the ion source by any other than some form of ionization gauge, because of the very low pressures involved. It is therefore common practice to establish a constant flow of sample vapour through a capillary or sinter into the ion source from a reservoir of the sample gas maintained at a higher pressure. The sample pressure in the reservoir and hence the pressure in the ion source remain substantially constant during the time in which measurements are made. Once the instrument has been calibrated by measuring the sensitivities on selected m/e values for pure sample vapours the analyst is in a position to deal with any mixture of those compounds for which he has recorded sensitivities. For every component in the mixture the analyst must measure the intensity of one ion current or peak height in the mixture spectrum. While it is sometimes possible to calculate the mixture composition by a spectrum-stripping technique, a more general method is to express the values of the ion currents or peak heights as sums of the products of sensitivities and partial pressures, obtaining a series of linear simultaneous equations and to invert the matrices. For complex mixtures this is best carried out by computer. It is sometimes impossible to carry out this routine because the resolution of the instrument is not sufficient to enable separation of ion currents at closely similar m/e values. If this is the case then a solution to the problem is to record two spectra of the mixture, one before and one after the quantitative conversion of one of the components of the mixture into a second substance. As an example the masses of carbon monoxide and nitrogen differ only by 1 part in 2800 and if the instrument available cannot achieve this resolution then a low-resolution spectrum is recorded and then the sample vapour in the inlet system is exposed to iodine pentoxide which converts the carbon monoxide into carbon dioxide quantitatively. A second spectrum is then recorded and in this spectrum the ion current at mass 28 is due only to nitrogen. From a comparison of the two spectra the concentration of carbon monoxide can be deduced.[30]

Analyses such as those described can only be carried out if a few milligrams of the sample are available and if the sample is sufficiently volatile to permit the achievement of suitable reservoir pressures. Much modern mass spectrometry is carried out, however, with solid samples of low volatility and these are normally analysed by introducing them directly into the ion source on the end of a ceramic or glass probe which is inserted into the instrument through a vacuum lock and within a few mm of the ionizing electron beam. In the most recent developments the probe may be heated or cooled to control evaporation. The resulting vapour molecules move only a short distance before they become ionized and so substances with extremely low vapour pressures may be analysed. Under these circumstances the sample pressure within the source is controlled only by the rate of evaporation and can only be adjusted crudely by altering the temperature or the position of the sample. It is thus not easy to calibrate the instrument or to analyse quantitatively. Further, since sample sizes have tended to diminish, the sample pressure may vary widely during evaporation, owing to the exhaustion of the solid on the probe. For this reason an alternative system has been devised in which the ion current due to the sample is integrated while the whole of a known amount of the sample is being evaporated. It is then possible to relate the integrated ion current to the amount of sample evaporated and to determine a sensitivity for the instrument with that sample.[31] One method of doing this would be to scan the whole mass spectrum repetitively at as rapid a rate as possible, while evaporating the sample, and to measure the corresponding peak height on each scan and plot peak height against time for each significant *m/e* value. This is possible experimentally and Fig. 7 shows the results of such a determination, using 60 ng of *p*-tyramine as the sample. The total evaporation time is about 100 sec. However, the recording of a large number of spectra is an expensive process and measurement of the spectra is tedious. The system only becomes practical if the mass spectrometer output is digitized and stored either on tape or in a core for processing by computer.

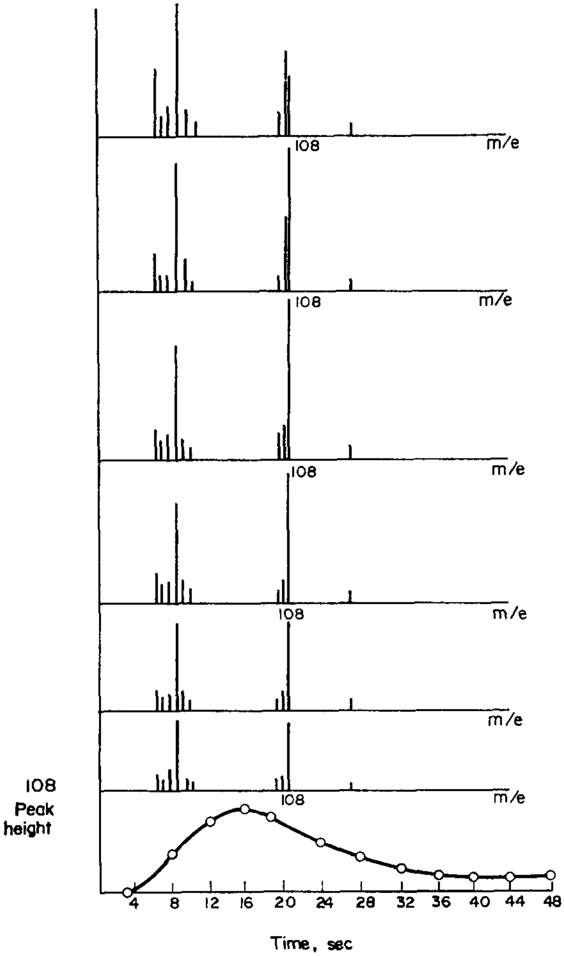


FIG. 7.—Mass spectrum scanned at 8-sec intervals during the evaporation of 60 ng of *p*-tyramine.

However, a compromise may be made in which not all of the spectrum but only a small part of it is repetitively scanned during the course of evaporation. The simplest possible situation is when only one ion current is recorded, for example the molecule ion-current since that will give most information about the molecule, although the argument would apply with equal force to a characteristic fragmentation peak in the mass spectrum. If the instrument is tuned to the selected *m/e* value before the evaporation begins and the ion current is recorded during the whole course of the evaporation of a small sample, then the record of the ion current at the selected *m/e* value is a measure of the rise and fall of the sample vapour concentration in the ion source, and the area under the curve so obtained is directly proportional to the integrated ion current and hence to the weight of sample evaporated. Thus an inexpensive and greatly simplified record is obtained and computer analysis is unnecessary. The problem of tuning in to a specific *m/e* value before an ion current is established at this value, *i.e.*, before evaporation has begun, is not always a simple matter. If voltage scanning, time-of-flight or radiofrequency instruments are being used, it is not too difficult, but with magnetic sector instruments without a very accurate mass-marking system it may not be possible to achieve. Further, it is often the case that an instrument of the latter type will go off tune during the course of an evaporation. For these reasons a system has been developed in which the single mass is repetitively scanned by means of peak switching facilities. Since this may be carried out in about 1 sec, only a short inexpensive recording is required and this consists of a series of peaks, the heights of which are proportional to the instantaneous ion current at the selected *m/e* value. These peaks rise and fall as the evaporation proceeds and it is the envelope of these peaks which constitutes the integrated ion current curve. Further, it is the area under this envelope which is proportional to the amount of sample evaporated. The problem of tuning to the *m/e* value with sector instruments may be solved by using a second calibrating substance in a second inlet system of the instrument, usually a reservoir of the type described above. The compound used is most commonly heptacosafluoro-tri-n-butylamine, which is allowed to flow into the source, and a peak in its spectrum is selected which is close to the *m/e* value which is being used for integration. This peak is then tuned in on the instrument by adjusting the magnet scan and the accelerating voltage is then altered so as to tune in the desired *m/e* value. The reference supply may then be cut off and evaporation initiated. If it is suspected that the sensitivity of the instrument is varying during the course of the evaporation then the ion currents due to the reference sample peaks may be recorded alternately with the sample peak currents. Any change in the height of the reference peaks would be due to a change in instrument sensitivity alone, since the sample source pressure of the reference compound is constant. In quantitative analysis by this technique the machine is first calibrated with known weights of pure samples of the compound. Comparison of the sample integrated ion-current curve area with the calibration graph gives a direct determination of the amount of unknown evaporated. Figure 8 shows such a calibration graph and it can be seen that there is linearity of response over several orders of magnitude. The limits of detection are very low indeed and detection of as little as 10^{-14} g has been achieved in favourable cases.[31] The effect of the matrix from which the sample is evaporated has been studied by making mixtures of two compounds, the major component being present in up to a million times the concentration of the minor component. It was found that provided the total sample size did not

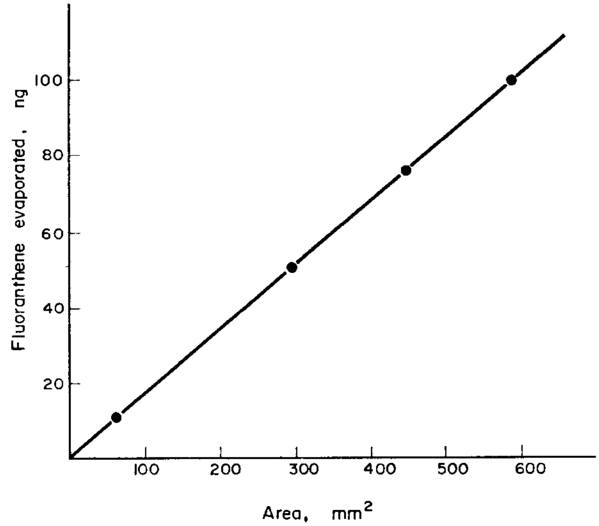


FIG. 8.—Calibration graph for fluoranthene.

exceed 5 μg, thus ensuring that the ion source pressure did not rise above 10^{-5} mm Hg, a plot of the integrated ion-current curve area for a characteristic *m/e* value of the minor component was linear down to the detection limit. The sensitivity of this technique varies with the compound and also with the characteristic *m/e* value selected. While it may be felt that the molecule ion peak is the most characteristic in the spectrum this sometimes carries only a very tiny fraction of the total ion current and thus can only give a low sensitivity. In such cases a characteristic fragment ion peak may provide a suitable *m/e* value for integration.

The analysis of metals

The most efficient method of analysing for trace metals is by the use of the spark-source double-focusing mass spectrometer such as the A.E.I. M.S. 7. Although the accuracy is limited by photoplate detection the ion currents due to all the ionized species are recorded at the same time and a limit of detection of one part in 10^9 has been claimed. Where the analytical requirements are less stringent it is sometimes possible to use the integrated ion current method with a general purpose mass spectrometer. Some metal salts such as mercuric chloride are themselves sufficiently volatile to permit their evaporation into the ion source directly. Figure 9 shows a portion of the mass spectrum for mercuric chloride, including the molecule ion region. It can be seen that the isotopic complexity has resulted in the distribution of the ion current over a number of isotopic ions and the sensitivity is thus much lower than that which can be achieved for a monoisotopic substance. However, amounts of mercuric chloride down to 1 ng can be determined with an error of 5%.[32]

Where no simple salt can be prepared it is necessary to convert the metal into a volatile form by making a chelate such as the acetylacetonate. The volatile nature of such chelates was first demonstrated by Morgan[33] over 40 years ago and more recently their properties have been exploited in an elegant and extensive study by Sievers,[34] using gas chromatography. The volatility of many metal chelates is improved by

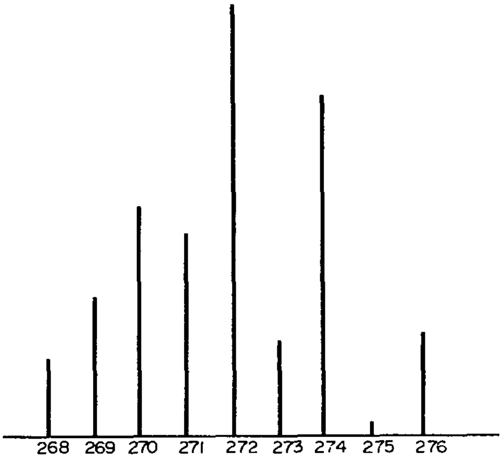


Fig. 9.—Mass spectrum of mercuric chloride.[32]

the substitution of fluorine and sulphur atoms in the diketone molecule. Although it is debatable whether alkali metal derivatives of diketones and keto esters can be classified as chelates, they may be evaporated from a probe into the ion source at temperatures below 200°.[35] Although it is possible to detect very small quantities of these compounds by the integrated ion current method the procedure is complicated by the fact that alkali metal chelates undergo two types of reaction upon evaporation—association and exchange.[36] Thus the mass spectra exhibit ions of the form $M_xL_y{}^+$ and the introduction of a large amount of a sodium chelate followed by, for example, a potassium derivative of a second diketone may result in the production of a spectrum revealing ions in which the two alkali metals have exchanged diketones. More complex association reactions are revealed if the chelates of alkali and alkaline earth metals are evaporated together.[37] Double chelates of the form $MM'L_3$ have been shown to exist. In the absence of the alkali metals however it is possible to estimate as little as 10^{-9} g of alkaline earth metals as their chelates with trifluoro-5,5-dimethylhexan-2,4-dione even though the mass spectrum exhibits polymeric peaks. Similar association reactions have been shown to occur between the chelates of alkali and rare-earth metals with the formation of binary chelates having the general formula $MM'L_4$.[35] In the absence of the alkali metals, however, very small quantities of rare-earth metals may be estimated as their chelates with heptafluoro-7,7-dimethyloctan-4,6-dione by the integrated ion current method.

1,3-Diketones or keto-esters have been used to make volatile derivatives of a number of other metals, the most volatile of these being the transition metal chelates, and detection limits for these species in the subnanogram range have been claimed. The power of the integrated ion current technique is, however, best demonstrated by the determination of mixtures of zirconium, hafnium and titanium as their trifluoroacetylbenzoylmethane chelates at the nanogram level–a formidable task by any other method.[39] There are many other chelating agents which form metal derivatives sufficiently volatile for their ready evaporation into the ion source and among these are 8-hydroxyquinoline, dipyridyl, dimethyl- and phenylglyoxime and the thio and amino derivatives of acetylacetone. A notable exception to this list is benzoylphenylhydroxylamine which forms derivatives which are not sufficiently stable to survive evaporation.

The integrated ion current method has been applied to the determination of a variety of organic compounds. It is perhaps very well suited to the analysis of polycyclic hydrocarbons obtained as air pollutants from automobile exhausts or the soot of smoky flames. The limit of detection for compounds such as the benzpyrenes is several orders of magnitude lower than that of any other technique. Further the spectrum of a complex mixture may be reduced to a number of molecule ion peaks by reducing the ionizing electron voltage to about 10 eV. Drugs have been assayed in blood and urine, and the distribution of non-catecholic amines in the human brain has been plotted.

A final feature of the integrated ion current technique is provided fortuitously by the differential rates of evaporation of closely similar compounds from the surface of a mass spectrometer probe. If the sample consists of a pair of isomers such as for example *o*- and *p*-nitrophenol, and if the curve is plotted for the molecule ion, then instead of the gaussian curve obtained for most sample evaporations a curve with two distinct maxima is obtained. This is because one isomer is being evaporated before the other. In all cases where isomerism can occur the integrated ion current curves have been shown to have fine structure. In the case of the chlorinated hydrocarbon "Chloran" no less than five maxima are visible. Structure has been demonstrated in curves obtained for *cis-trans* isomers, dioximes, polycyclic hydrocarbons, and very convincingly for metal chelates. By this means, the existence of *cis-trans* isomerism in the 8-hydroxyquinoline derivatives of bivalent metals has been demonstrated and complete separation of the isomers has been achieved in the 8-hydroxyquinoline derivatives of tervalent metals.[40]

An interesting application of the integrated ion current technique is in the assessment of the efficiency of decontamination agents and the cleaning of surfaces. For this application the probe is replaced by a small cylinder made of the material on which decontamination studies are to be made. The surface is then coated with a substance which is sufficiently volatile to be evaporated into the ion source at a high temperature. The amount adhering is determined in the normal way. The probe is then recontaminated and before assay is washed in the appropriate decontamination agent. The amount remaining is then assayed as before.

In the original study it was found that washing in cold solutions of efficient decontamination agent removed the contamination down to the level where it existed as a monolayer on the surface. This monolayer was only removed by treatment with the agent at elevated temperatures. More recently a phosphate-free decontamination agent, Decon 90, has been shown to break through the monolayer even in the cold and to leave no detectable film of contamination on the mass spectrometer probe after treatment at 50°.

Zusammenfassung—Es wird ein Überblick über die elementare Theorie, die Technik und die Anwendung der Massenspektrometrie gegeben. Besonders wird auf apparative Entwicklungen und dadurch bedingte neue Anwendungsmöglichkeiten hingewiesen.

Résumé—On a effectué une revue de la théorie fondamentale, de l'instrumentation et de l'application de la spectrométrie de masse, spécialement en ce qui concerne le développement de l'équipement et sa répercussion sur le cadre l'application.

REFERENCES

1. J. R. Majer, R. Perry and M. J. Reade, *J. Chromatog.*, 1970, **48**, 328.
2. J. R. Majer, W. D. Capey and J. C. Robb, *Nature*, 1964, **203**, 294.
3. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, Elsevier, Amsterdam, 1960.
4. F. W. McLafferty, *Mass Spectrometry of Organic Ions*, Academic Press, New York, 1963.
5. J. R. Majer, *Advances in Fluorine Chemistry*, Vol. II, p. 55, Butterworths, London, 1961.
6. B. G. Gowenlock, J. Kay and J. R. Majer, *Trans. Faraday Soc.*, 1963, **59**, 2463.
7. F. W. McLafferty, *Interpretation of Mass Spectra*, Benjamin, New York, 1966.
8. J. R. Majer and C. R. Patrick, *Nature*, 1961, **192**, 866.
9. J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1861.
10. K. R. Jennings, *Proceedings of Symposium on Some Newer Physical Methods in Structural Chemistry, Oxford, 1966*, p. 105, London United Trade Press, London, 1967.
11. H. D. Beckey, *Z. Naturforsch.*, 1959, **14a**, 712.
12. M. S. Munson and F. H. Field, *J. Am. Chem. Soc.*, 1966, **88**, 2621.
13. O. A. Koleoso, S. M. C. Dietrich and R. O. Martin, *Biochemistry*, 1969, **8**, 4172.
14. J. H. Beynon and A. E. Fontaine, *Instr. Rev.*, 1967, 470.
15. A. J. Dempster, *Phys. Rev.*, 1918, **11**, 316.
16. A. O. Nier, *Rev. Sci. Instr.*, 1940, **11**, 212.
17. J. Mattauch and R. F. K. Herzog, *Z. Physik.*, 1934, **89**, 786.
18. R. D. Craig and G. A. Errock, *Advances in Mass Spectrometry*, ed. J. D. Waldron, p. 66, Pergamon, Oxford, 1959.
19. A. O. Nier and E. G. Johnson, *Phys. Rev.*, 1953, **91**, 10.
20. H. Hintenberger and L. A. Konig, *Advances in Mass Spectrometry*, ed. J. D. Waldron, p. 16, Pergamon, Oxford, 1959.
21. W. Paul and H. Steinwedel, *Z. Naturforsch.*, 1953, **8a**, 448.
22. U. von Zahn, *Rev. Sci. Instr.*, 1963, **34**, 1.
23. E. Fischer, *Z. Physik.*, 1959, **156**, 1.
24. W. E. Stephens, *Phys. Rev.*, 1946, **69**, 691.
25. J. M. B. Bakker, *Proc. Intern. Conf. Mass Spectr.*, Brussels, 1970.
26. W. H. McFadden, *Advances in Chromatography*, ed. J. C. Giddings and R. A. Keller, Vol. 4, p. 265. Arnold, London, 1967.
27. D. I. Rees, *Talanta*, 1969, **16**, 903.
28. R. Ryhage, *Anal. Chem.*, 1964, **36**, 759.
29. J. T. Watson and K. Biemann, *ibid.*, 1964, **36**, 1135.
30. J. R. Majer, *Talanta*, 1970, **17**, 1970.
31. A. E. Jenkins and J. R. Majer, *ibid.*, 1967, **14**, 777.
32. J. R. Majer, *ibid.*, 1969, **16**, 420.
33. G. T. Morgan and F. H. Burstall, *Inorganic Chemistry, A Survey of Modern Developments*, Heffer, Cambridge, 1936.
34. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
35. R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, *Anal. Chim. Acta*, 1969, **45**, 305.
36. J. R. Majer and R. Perry, *Chem. Commun.*, 1969, 271.
37. *Idem, ibid.*, 1969, 454.
38. R. Belcher, J. R. Majer, R. Perry and W. I. Stephen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 471.
39. M. G. Allcock, R. Belcher, J. R. Majer and R. Perry, *Anal. Chem.*, 1970, **42**, 776.
40. J. R. Majer and M. J. A. Reade, *Chem. Commun.*, 1970, 58.

Talanta, 1972, Vol. 19, pp. 623 to 639. Pergamon Press. Printed in Northern Ireland

DEVELOPMENT AND PUBLICATION OF WORK WITH SELECTIVE ION-SENSITIVE ELECTRODES

G. J. MOODY and J. D. R. THOMAS
University of Wales Institute of Science and Technology, Cardiff, Wales

(*Received* 7 *July* 1971)

Summary—Features concerning development, response, selectivity and applications of selective ion-sensitive electrodes are reviewed. Recommendations are made concerning investigations involving the development and applications of electrodes and attention given to the manner of presenting data for publication.

OVER SIXTY YEARS have elapsed since the initial discovery[1] and characterization[2] of the electrical potential arising at a thin glass membrane interposed between aqueous solutions of different acidity, but it is only within the last five or six years that there has been widespread development and interest in sensor membrane electrodes based upon a more general application of ion-exchanging materials. This might seem surprising when viewed against the prediction by Lengyel and Blum[3] in 1934 of a cation-sensitive glass electrode and of reports by Tendeloo[4] in 1935 and Kolthoff and Sanders[5] in 1937 detailing potentiometric response to certain ions by electrodes composed of solid-state membranes of barium sulphate and calcium fluoride slices[4] or discs of silver halides.[5]

Glass electrodes selective to hydrogen ions have been standard items of laboratory equipment for over thirty years, but it was just over ten years ago that glasses of modified composition were adapted for selective response to cations other than hydrogen ions. As the advantages of a wider range of selectively sensitive electrodes were materializing, Pungor and Holós-Rokosinyi[6] described in 1961 the selective working of precipitate-based ion-sensitive electrodes. However, it was the commercial availability of the fluoride solid-state electrode[7] in 1966, which coincided with the tremendous interest in the determination of trace fluoride following water fluoridation and dental health programmes, that initiated the recent vast interest in selective ion-sensitive electrodes. Symposia such as those held in January 1969 at the National Bureau of Standards, Gaithersburg, Maryland, U.S.A., and in February 1969 at the University of Wales Institute of Science and Technology, Cardiff, U.K., have boosted their general acceptance. The subsequent publication of the N.B.S. Symposium proceedings has provided a very useful source book[8] which has been well-supplemented by the Orion Research Incorporated Data Sheets and *Newsletter*.

The full benefit of selective ion-sensitive electrodes can only be realized by thorough familiarity with their properties and mode of operation. With this in view, this paper is intended to suggest a set of requirements in outlining the development, assessment and application of these electrodes. This is felt to be necessary in view of the existing ambiguities concerning the relation of potential to the logarithm of the activity of active ion and presentation of selectivity ratios or coefficients. Further reasons involve lifetimes and response time under various operating conditions. While it is recognized that different opinions and individual preferences will still flourish, it is nevertheless hoped that a format can be developed for the convenient presentation of results that will permit ease of assimilation and realistic appraisal by other workers.

DEVELOPMENT OF NEW ELECTRODES

Potential response

In general, the potentiometric cell assembly incorporating a selective ion-sensitive electrode takes the form shown in Fig. 1 where the e.m.f., E, of the cell is the sum of various junction potentials:

$$E = E_M + E_{M'} + E_R + E_{R'} + E_j \tag{1}$$

Except for E_M, which depends on the nature of the test or standardizing solution, the remaining contributory potentials may be taken as constant, although some of the junction potentials, particularly those of the reference electrode, can be troublesome. The reference electrode used in any investigation should be specified in published reports, along with the model and impedance of the e.m.f.-measuring instrument.

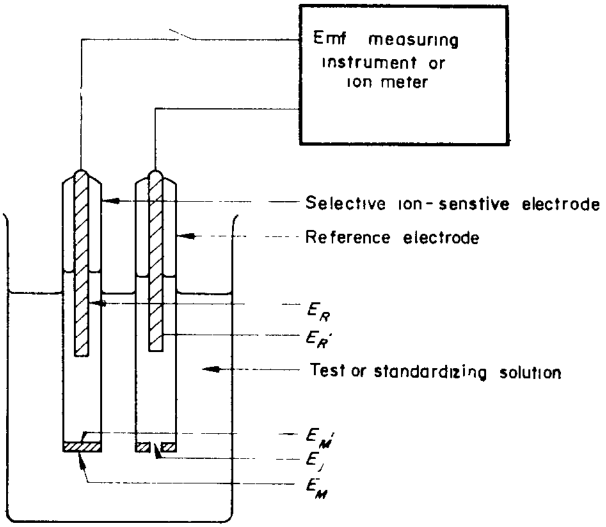


FIG. 1.—Experimental circuit for using selective ion-sensitive electrodes.

For an electrode responding selectively to an ion, i, of activity a_i and charge z, in the presence of an interfering ion, j, of activity a_j and charge y, E, for Nernstian response, is given by

$$E = \text{constant} \pm \frac{2{\cdot}303RT}{zF} \log \left[a_i + K_{ij}(a_j)^{z/y}\right] \tag{2}$$

where K_{ij} is the selectivity coefficient. The constant term incorporates the various junction potentials and the standard potential characteristic of E_M. The second term on the right-hand side of equation (2) takes the positive sign for cations and the negative for anions.

On the basis of the response characteristics above, selective ion-sensitive membrane electrodes have been described for about twenty ions which are fairly evenly divided between cations and anions. There is, therefore, plenty of scope for fresh developments, both for electrodes selectively sensitive to an extended range of ions and for improvements and refinements to existing electrodes.

Unless the electrode is going to be available commercially, its description should carry exact details for its construction, and the design need not be any more intricate than the minimum necessary for the performance claimed.

The dependence of the e.m.f. response on the logarithm of the activity indicates [equation (2) in the absence of interferent] that E will alter by only 2·72 mV for a univalent ion and by 1·36 mV for a bivalent ion for a 10% decrease in the activity of the active species and by only 2·45 mV for a univalent ion and by 1·23 mV for a bivalent ion for a 10% increase in the activity of the active species. These figures mean that a sensitive voltmeter (with high impedance to cope with the high resistances involved) responding to 0·1 mV, or better, is recommended[9] for work of acceptable precision. Expanded scale facilities on commercial pH-meters do not normally meet this requirement.

Selectivity

Membrane electrodes have the advantage that they can be tailor-made for almost any ion, but the difficulty of distinguishing adequately between different ions, particularly of the same sign, is a serious limitation. Hence, considerable effort has been devoted to assessing the performance of the new range of electrodes in the presence of possibly interfering ions. This has been done in terms of the selectivity coefficients, K_{ij}, defined by equation (2), the methods employed[9,10] for evaluating K_{ij} being based on e.m.f. measurements either in separate, or more realistically in mixed, solutions of the primary ion, i, and interfering ion, j.

The two separate-solution methods with the solutions producing e.m.f.s E_1 and E_2, involve either equation (3) or (4) depending, respectively, on equality of the primary and interferent ion activities and of the e.m.f.s:

$$\pm\left(\frac{E_2 - E_1}{2{\cdot}303RT/zF}\right) = \log K_{ij} + \left(\frac{z}{y} - 1\right)\log a_i \tag{3}$$

$$a_i = K_{ij}(a_j)^{z/y} \tag{4}$$

For cations, the left-hand side of equation (3) takes the positive sign, and the negative sign for anions. The second term of the right-hand side disappears when the charges of the primary and interfering ions are equal.

Separate solutions are not typical of operating systems so a more common procedure for assessing selectivity ratings is measurement of the e.m.f. in solutions containing a fixed amount of interferent with varying activities of the primary ion for which the electrode is designed. Figure 2 illustrates the general idealized pattern and the calculation of K_{ij} from equation (4).

It is pertinent at this point to stress the benefits[11] of the universal and consistent adoption of K_{ij} as described above for listing selectivity data. The inconsistencies to date, particularly in some manufacturers' literature, can only cause bewilderment to readers and users alike. Such a system of presenting selectivity data consistently indicates that when $K_{ij} < 1$ the electrode preferentially responds to the primary ion, i. However, Fig. 3 stresses the care needed in any interpretation of any single published item of selectivity information, for selectivity varies with the relative primary ion/interferent activities. Thus, for the poly(vinylchloride) calcium-sensitive electrode[12] the value $K_{\mathrm{CaMg}} = 0{\cdot}024$ obtained at a high magnesium content ($a_{\mathrm{Mg}} = 5 \times 10^{-3}M$)

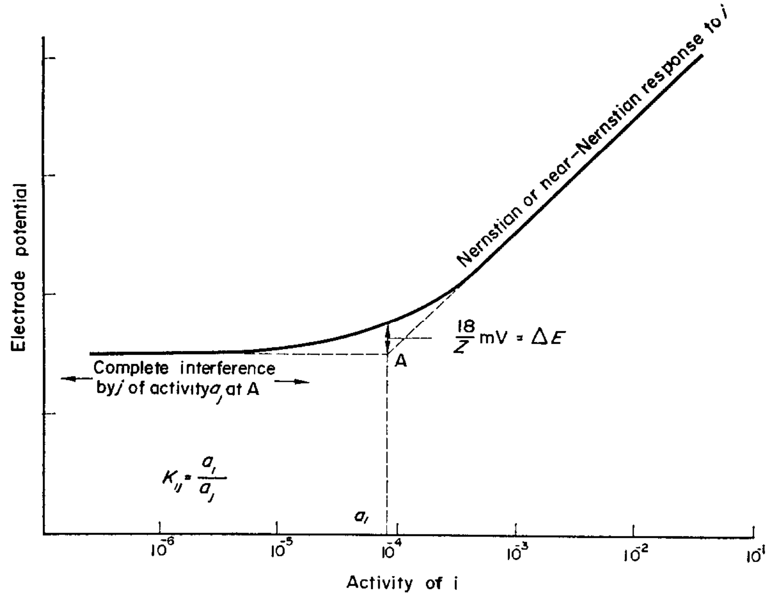


FIG. 2.—Illustration of selectivity coefficient evaluation, using fixed initial amount of interferent of same valence as *i*.

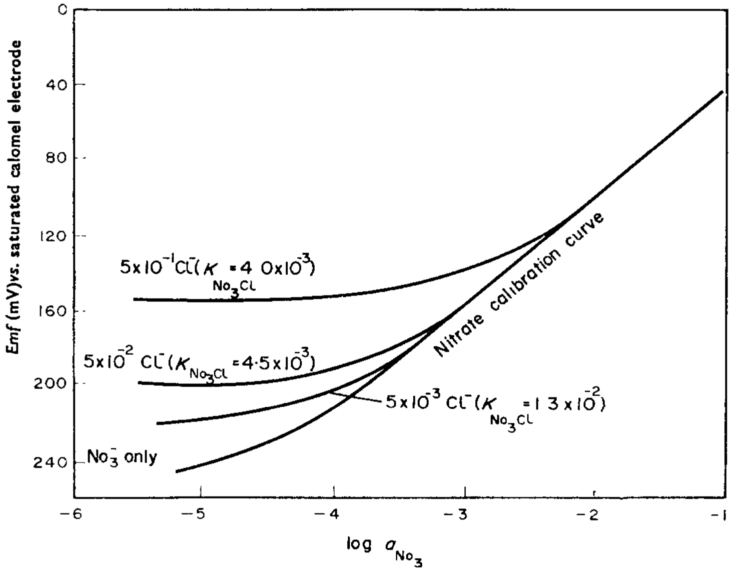


FIG. 3.—Influence of chloride on the response characteristics of a nitrate-sensitive (Orion 92-07-02 nitrate liquid ion exchanger) poly(vinylchloride) electrode.

suggests a better selectivity than $K_{CaMg} = 0{\cdot}222$ at a lower magnesium level ($a_{Mg} = 4{\cdot}3 \times 10^{-5}M$), while in fact the electrode gives the most extensively useful response at lower magnesium levels (*cf.* Fig. 3 for a nitrate-sensitive electrode affected by chloride interference).

The considerable variation of selectivity with interferent concentration is further illustrated by the work of Lal and Christian[13] on fifteen foreign cations, using the Orion 92–82 lead electrode. However, the apparent lack of critical assessment in this paper[13] emphasises the attention to detail essential for studies on electrode assessment. Thus, in commenting that the Orion lead electrode is much more responsive to univalent cations than is reported by the manufacturers, Lal and Christian[13] have not considered the modifying influence of the power term of equation (4). Yet this equation shows that the lead electrode has nearly the same useful range in the presence of $10^{-5}M$ sodium (down to $8{\cdot}9 \times 10^{-4}M$ lead) as it has in the presence of $10^{-5}M$ calcium (down to $2{\cdot}5 \times 10^{-4}M$ lead) even though the respective K_{ij} values differ by several orders of magnitude ($K_{\mathrm{PbNa}} = 8{\cdot}9 \times 10^6$ and $K_{\mathrm{PbCa}} = 25$). The extensive useful range permits the lead potentiometric titrations mentioned by these workers[13] but a high response to the sodium and potassium salt titrants used would hardly permit such an application. Moreover, potentiometric titrations of various univalent cations with sodium tetraphenylborate, with the lead electrode as sensor, warrant further investigation to determine the true mechanism.

The importance of the useful role of plots such as Fig. 3 for investigations involving interference parameters cannot be over-emphasized. Unfortunately, however, such plots take up journal space and where the mixed-solution method[9,10,13] has been employed, an alternative procedure[11] is to quote the activity, a_j, of the interfering ion corresponding to each K_{ij} value. Readers will then be realistically informed that should the level of j in the test situation exceed this value and the expected activity level of i be less than $K_{ij}(a_j)^{z/y}$, then the electrode will very likely be useless in such a test situation.

An alternative mixed-solution method of expressing selectivity involves variation of interferent activity at constant primary ion activity[9,10,14] and is generally used for assessing hydrogen ion and hydroxide ion interference. Several diagrams expressing constancy of e.m.f. response over a pH range have been published[12,15,16] and these confirm that unless there are unusual features it is adequate to quote a pH range for which there is unlikely to be interference with electrode behaviour, but again it is essential to quote the level of primary ion for that pH range.

Srinivasan and Rechnitz[10] considered neither of the foregoing mixed-solution methods in their treatment of potential data obtained for several different Orion liquid membrane ion-sensitive electrodes. Instead, two rather complicated equations were proposed, the general form of the one for high values of K_{ij} being

$$\left[\exp \pm\left(\frac{E_2 - E_1}{RT/zF}\right)\right]a_i - a_i' = K_{ij}(a_j')^{z/y} \tag{5}$$

and that for low values of K_{ij} being

$$a_i' - \left[\exp \pm\left(\frac{E_2 - E_1}{RT/zF}\right)\right]a_i = K_{ij}\left[\exp \pm\left(\frac{E_2 - E_1}{RT/zF}\right)(a_j)^{z/y} - (a_j')^{z/y}\right] \tag{6}$$

As before, the positive sign alternative is used for cation-sensitive electrodes and the negative for anion-sensitive electrodes. The a values refer to E_1, the a' values to E_2.

Equation (5) is used by plotting the left-hand side against interferent activities, a_j', and equation (6) is used by plotting the left-hand side against the square-bracketed function of the right-hand side. In each case, linear plots are obtained, of slope K_{ij}.

However, there is little to commend such complicated functions when the desired information concerning the potential applicability of electrodes can so conveniently be obtained from plots of the kind shown in Fig. 3.

Selectivities of solid-state electrodes have been variously expressed and emphasize the present chaos regarding selectivity quotations.[11,14] Except for the method involving equations (5) and (6), the practical methods employed for evaluating the selectivities are those already described above, although Light and Swartz[17] used equation (5) in a non-graphical procedure for determining anion interferences for the Orion 94-16 sulphide electrode.

The interference mechanism of solid-state electrodes differs from that of liquid ion-exchange and glass electrodes in the manner in which the primary ion and interfering ion(s) gain access to the all-important membrane.[14] This has led to criticism by Pungor and Tóth[18] concerning the application of the methods above for determining the selectivities of precipitate-based selective ion-sensitive electrodes. Even so, these workers used equation (4) in its appropriate form for obtaining "measured" selectivities of halide electrodes for comparison with those calculated from solubility product ratios.[18] This, of course, highlights a common form of interference of crystal membrane and precipitate-impregnated membrane electrodes, arising from the interfering ion actually reacting at the membrane surface to form a new insoluble compound.[19] For this kind of interference, a knowledge of solubility products of the membrane salt and of the insoluble compound formed is helpful in predicting the usefulness of an electrode. For example, for thiocyanate interference with the silver bromide electrode, the selectivity ratio, K_{BrSCN}, is given by the ratio of the solubility product of silver bromide to the solubility product of silver thiocyanate. This implies that for the electrode to be functional to bromide in the presence of thiocyanate, the ratio of the interfering thiocyanate to the primary bromide activity must not exceed the ratio (solubility product of AgSCN)/(solubility product of AgBr). Of course, the inverse relationship holds when the electrode is to be used for thiocyanate, with bromide interference, the form[11] of the selectivity ratio then being K_{SCNBr}.

Interference with solid-state electrodes also occurs when the membrane material reacts with interferent to give a soluble complex, a feature that has been exploited in adapting silver halide membranes for use as cyanide electrodes.[18,20,21] Dissolution of the membrane is also regarded as the basis of the "high" fluoride readings[14,22] obtained with the lanthanum fluoride electrode in the presence of citrate in dilute fluoride solutions.

Activity and ionic strength

The various equations for calculating selectivity coefficients depend upon a knowledge of activities and it follows that consistency and exact reporting of selectivity data ought also to include outline information on the calculation of the activity coefficient, f, which is used to calculate activity from concentration. Such information is especially desirable since the Debye-Hückel equation,

$$\log f = -Az^2\sqrt{\mu} \tag{7}$$

where A is a constant which for water is 0·511 at 25°, holds strictly only for zero ionic strength, μ, and its predictions differ from the behaviour of real electrolytes at ionic strengths greater than 10^{-3}–$10^{-2}M$. To meet this situation a variety of more or less empirical extensions to equation (7) have been proposed to fit the data (with varying success) at moderate values of ionic strength (Fig. 4).

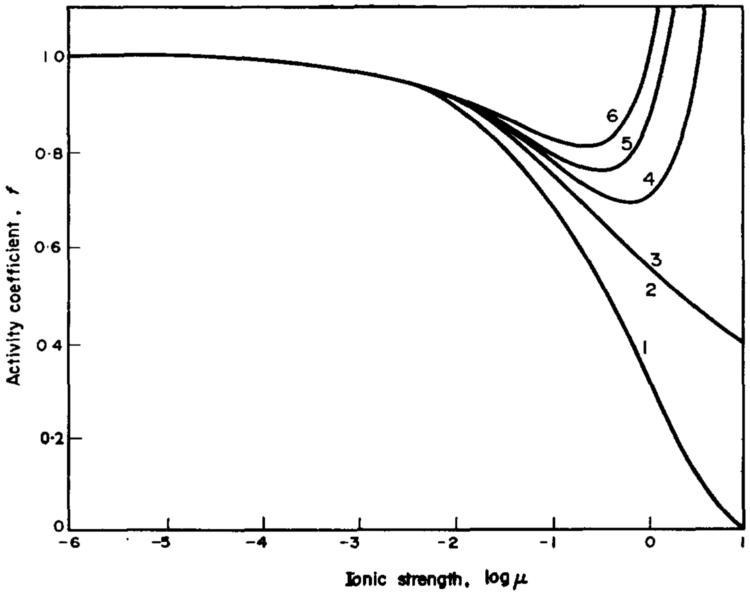


FIG. 4.—Computer simulations of various activity coefficient-ionic strength equations for univalent ions.

1. $\text{Log} f = -Az^2\sqrt{\mu}$

2. $\text{Log} f = \dfrac{-Az^2\sqrt{\mu}}{(1 + \sqrt{\mu})}$

3. $\text{Log} f = \dfrac{-Az^2\sqrt{\mu}}{(1 + 0{\cdot}329R\sqrt{\mu})}$ (*R* taken as 3 Å)

4. $\text{Log} f = -Az^2\left[\dfrac{\sqrt{\mu}}{1 + 1{\cdot}5\sqrt{\mu}} - 0{\cdot}2\,\mu\right]$

5. $\text{Log} f = -z^2\left[\dfrac{A\sqrt{\mu}}{1 + \sqrt{\mu}} - 0{\cdot}2\,\mu\right]$

6. $\text{Log} f = -z^2\left[\dfrac{A\sqrt{\mu}}{1 + 1{\cdot}5\sqrt{\mu}} - 0{\cdot}2\,\mu\right]$

The variation of the Debye-Hückel equation shown in equation (8) is extensively used in selective ion-sensitive electrode work for calculating the single ion activity:

$$\log f = -\frac{Az^2\sqrt{\mu}}{(1 + \sqrt{\mu})} \tag{8}$$

The ionic strength, μ, is given by

$$\mu = \tfrac{1}{2}\sum cz^2 \tag{9}$$

where c and z are the concentration and charge respectively of each ionic species present.

Stability of response

Closely related to selective response in the rating of ion-sensitive electrodes is drift and response time. Reports on steadiness and reproducibility of electrode response can provide useful guides to prospective users on frequency of recalibration and the suitability of the electrode for continuous process use.

Electrodes of different types are liable to different extents of drift, although wider drifts necessitating frequent recalibration can be tolerated when alternative methods of analysis are cumbersome or non-existent. Some electrodes have very low drift, *e.g.*, a potassium electrode with biological membrane (Beckman Catalogue No. 39622) for which daily checking during a continuous ten-day soaking period in $10^{-2}M$ potassium chloride "did not produce a noticeable drift."[16] However, an accompanying table does show differences in response of up to ± 2 mV after ten days, compared with the initial response.[16] No results are quoted for the intervening period, although the ten-day results cover the potassium concentration range 10^{-5}–$10^{-1}M$ ($9{\cdot}96 \times 10^{-6}$–$7{\cdot}7 \times 10^{-2}M$ activity).

Data[22–24] for the well-established and widely used lanthanum fluoride crystal membrane fluoride-responsive electrode indicate a similar ± 2 mV drift for the Orion 94-09 model, although Srinivasan and Rechnitz[25] report drifts of up to 7 mV depending on stirring and activity conditions, the response being steadier at high ionic strengths.

Miniaturization of electrodes is desirable for *in vivo* measurements or for *in situ* studies where solution volume is a limitation.[26] However, design demands can lead to specification change and for this reason reports should clearly specify electrode types used. Thus, for a fluoride microelectrode[26] the zero potential varied by about ± 20 mV from day to day but, on the other hand, depth of immersion had little effect on the potential, the e.m.f. shift being about -2 mV over the 1 mm length of the exposed lanthanum fluoride crystal.

While 2 mV drifts may seem insignificant, it must be emphasized that drifts of this magnitude can lead to errors of several per cent. Frequent recalibration of selective ion-sensitive membrane electrodes is therefore essential, especially for the liquid ion-exchanger membrane electrodes which are reported to have drifts of over 2 mV for a single day's use,[12,27,28] even extending to 70 mV for an Orion 92-07 nitrate electrode.[27] However, provided the calibration slope does not alter with time, recalibration is a simple matter and not a serious drawback, particularly when alternative analysis procedures are cumbersome or non-existent.

Calibration slopes

Equation (2) suggests that calibration slopes should be $59/z$ mV at 25°. For selective ion-sensitive electrodes this is far from universally true, although slopes are normally within 2–3 mV of the Nernstian value. This is no inconvenience so long as the particular calibration slope does not change with time, and unlike the overall drifts mentioned above, slopes have been found to be extremely steady during normal electrode life; if not, failure of the electrode is indicated.

A drastic change in slope can often be related to some malfunction of the reference electrode, whereas failure of a functional selective-ion sensitive electrode is more gradual, being manifested as a drop in calibration slope.

As with drifts, some very large deviations in calibration slope have been reported;

for example, slopes ranging from 64 to 50 mV per activity decade and attributed to defective assembly have been reported[27] for the liquid ion-exchanger Orion 92-07 nitrate electrode.

Deviations from Nernstian behaviour may be attributed to incomplete permselectivity of the membrane, a factor which Helfferich[29] covered by an integral term in the function for membrane potential to account for the co-ion flux. Such integrals may be evaluated graphically, but this is of no benefit in the present context and for general application here it is adequate to take a coefficient, S, instead of $2{\cdot}303RT/zF$ in equation (2), where S is the calibration slope.

Speed of response

Several studies have been made of the response times of selective ion-sensitive electrodes, principally by Rechnitz[30–34] and Pungor,[35] although descriptions of new electrodes frequently include details of response times.[12,16,28] In general, liquid exchanger ion-sensitive membrane electrodes respond less rapidly than the solid-state type.

It can be argued that rather too much emphasis has been placed on response times of electrodes; this is certainly the case for direct potentiometric determination of activity where response times of some minutes are quite tolerable. However, automatic analysers and continuous-measurement cells require sensors with more rapid response, and response times of minutes are too long for kinetic work and potentiometric titrations.

In attempts to determine very short response times, the relatively high time-constants of measuring instruments can be a limitation, but when electrodes with such ideal time responses have been achieved, there is no reason for obsession with this characteristic until the measuring instruments and the slow equilibration of junction potentials within the measuring-cell have been improved.

Response times are usually measured either by immersing the electrode in the solution and finding the time needed to reach equilibrium, or by injecting a solution of appropriate concentration into the system in which the electrode is already immersed. The equilibration can be monitored by chart-recorder, but Pungor[35] used an oscilloscope for times in the millisecond range. Response time data should be given for change from dilute to concentrated solution and for change in the opposite direction, and in addition, for reading within 1 mV of the equilibrium value. The latter times are usually a mere fraction of the full equilibration times and can provide guides for continuous monitoring and potentiometric applications. Indeed, where full equilibration times are long, the "1-mV times" can be short enough for rapid potentiometric titration rather than the intermittent start and stop of the burette system in automatic systems that is sometimes necessary[36] in order to allow equilibration near the equivalence point. However, there are few reports on response times in mixed solutions.

It is interesting that electrode response is very steady during stirring[12,16,25,33,34] and that base-line noise levels of recorders are only important at low activities.[16] However, there can be differences in potential response between stirred and unstirred solutions[25] and for different rates of stirring.[33,34] Differences of 0·4 and 6 mV have been observed[25] in the potential response of the Orion 94-09 fluoride electrode for

10^{-1} and $10^{-3}M$ fluoride solutions respectively, although at high ionic strengths, for example in $1M$ sodium nitrate, no such differences are evident.[25]

Conditioning and storage of electrodes

As with glass electrodes, the selective ion-sensitive electrodes often need conditioning before use. The description of any new electrode should specify any conditioning needed, particularly when there are unusual features such as the need to age the Corning Model No. 476132 potassium electrode in a solution having a composition simulating that of the test solution in order to avoid long response times and hysteresis effects.[37] Similarly, information should be given on the conditioning necessary to recover from detrimental circumstances; for example, liquid ion-exchanger calcium electrodes take an hour to regain proper response potentials to pure calcium chloride solutions after exposure to zinc chloride[12] and, after exposure to perchlorate, nitrate electrodes take almost as long to return to normal behaviour.[28] Silver thiocyanate should be removed from the membrane (by wiping or with a toothbrush and toothpaste) of silver bromide electrodes after exposure to interfering levels of thiocyanate.[38]

Storage conditions for electrodes when not in use should also be stated.

APPLICATION OF SELECTIVE ION-SENSITIVE ELECTRODES

The recent interest in selective ion-sensitive electrodes has resulted in about 400 papers devoted to development and uses. A large proportion concern the specification and appraisal of electrodes, but as the rate of appearance of new electrodes might be expected to diminish, it can be expected that an increasing proportion of future publications will be devoted to application and mechanism.

It is therefore necessary to specify which factors must be examined in development of an application, and what information must be given in any paper published on the work done.

The applications are generally to direct determination of activity (or concentration), or to titration procedures.

With adequate attention to calibration, particularly at low concentration levels and low ionic strength, selective ion-sensitive electrodes may be used for direct concentration measurements.

In using membrane electrodes, precautions must therefore be taken against complications at high concentrations and due to other ionic species with respect to variation of activity with ionic strength. Interference effects must also be tested at realistic levels. For example, bearing in mind equation (4), there is *no* point in attempting to use a nitrate electrode with selectivity coefficient $K_{\mathrm{NO_3Cl}} = 4 \times 10^{-3}$ determined for a chloride level of $0{\cdot}5M$, when assessing soil nitrate in concentrations of about $10^{-4}M$, when $2M$ potassium chloride is the extracting agent. This is evident from Fig. 3, which confirms that the response would be constant regardless of the nitrate activity. However, $0{\cdot}01M$ copper sulphate or water could be used as extractant,[40] although saline soils high in chloride might require supplementary treatment.

Both the Øien[40] and Milham[41] papers on soil nitrate determination are thorough in their enquiry and can serve as models for this kind of publication, although the former tends to include ambiguous statements. Both give due attention to comparisons with established methods, recovery, a wide variety of samples, and the limitations of published selectivity coefficients and of making corrections by equations, which for complicated systems of this kind would demand selectivity terms additional to the single one given in equation (2). Hence, Milham *et al.*[41] used rather an involved buffer system to cope with some interferents: a low pH kept the equilibrium bicarbonate low and the water-extractable organic acids undissociated; aluminium was added to complex anions of organic acids, and sulphamic acid was used to destroy nitrite quantitatively.

Both papers also pay attention to possible effects of ionic strength, and give information on electrode conditioning and mixing times before measurement. The inclusion of the correlation coefficient and regression equation is also valuable.

Concentration measurements of uncomplexed ions

Exhaustive examination of the effect of ionic strength is necessary for appraisal of the application of selective ion-sensitive electrodes. Conductance monitoring may not give satisfactory guidance—possibly because of the power term in z in equation (9). Though direct measurement on the sample can give acceptable results, it is only when a sample consists largely of one salt that an activity–e.m.f. calibration plot can be used accurately. However, such a plot may be acceptable for mixed solutions if the ratio of the primary ion to that of the other ions is constant. For example, to estimate potassium in sea-water, calibration standards are made by diluting synthetic potassium sea-water samples with demineralized water.[14]

The constant ionic-background method is frequently used when the analytical sample contains a high but essentially constant level of ions besides the one of interest. Calibration standards of similar composition are then employed, but ions at interfering levels must be absent, of course.

If samples exhibit considerable overall variation in composition, adding an "ionic strength adjuster" to the sample and calibration solutions tends to bring all the solutions to a common ionic strength. It is assumed that the ultimate ionic strength arises almost exclusively from the ionic strength adjuster and not the sample itself. This is the basis of the involved buffer system[41] described above for nitrate determination in various materials, although the buffer was also a judicious recipe to meet the selectivity parameters of the electrode. Though virtually any substance may serve as an ionic strength adjuster, it must not complex with the primary ion, and the selectivity coefficient, K_{ij}, where j is the ionic strength adjuster, must be negligible. Tetramethylammonium nitrate was chosen for this reason for an investigation[42] of calcium complexes with tri- and tetrametaphosphate, using a calcium-selective liquid ion-exchange membrane electrode. Certain variations may sometimes be necessary in addition to ionic strength adjustment, for example, pH adjustment will release anions of weak acids. Thus, at pH 10·5 the cyanide ion is present and not undissociated hydrocyanic acid.[35]

Measurements of total concentration

The methods just discussed give the concentrations (or activities) of free (that is, uncomplexed) ions. These may be quite different from the total concentrations (that is, free + complexed species). Two elegant methods are now available for total concentration measurements.[43,44,45] Electrode calibration is not usually necessary and only two potentials need be taken.

Both methods require a change in the concentration of the primary ion, *i*. For *known addition* (otherwise known as the *spiking* or *known-increment method*) more *i* is introduced, whereas in *known subtraction* the level of *i* is lowered by adding a complexing agent. There are no complications from ionic strengths as in the previous cases.

In the known-addition method, the potential, E_1, is measured for the sample solution of volume V_0 and total molar concentration C_0 of species sought,

$$E_1 = \text{constant} \pm S \log x_1 f_1 C_0 \tag{10}$$

where S is the electrode calibration slope, f_1 is the activity coefficient and x_1 the mole fraction of uncomplexed ions. A new potential, E_2, is then measured after addition of a small volume, V_A, of a standard solution (concentration C_s) of ions of the species sought where $C_s \sim 100C_0$:

$$E_2 = \text{constant} \pm S \log (x_2 f_2 C_0 + x_2 f_2 C_\Delta) \tag{11}$$

where f_2 and x_2 correspond to the new activity coefficient and mole fraction of free ions, respectively, and C_Δ is the change in concentration, given by $V_A C_s / V_0$. An essential assumption is that $x_1 \sim x_2$ and $f_1 \sim f_2$. Hence the difference between equations (10) and (11) simplifies to

$$E_2 - E_1 = \Delta E = \pm S \log \left(\frac{C_0 + C_\Delta}{C_0}\right) \tag{12}$$

and C_0 can be calculated.

A variation of the known addition method has recently been recommended[46,47] and is based on a modification of the method described by Gran[48] for presenting potentiometric titration data in linear form by using a semi-antilog plot. The method[47] involves plotting the appropriate potential response on the vertical antilog axis against volume (ml) of "known addition" with the intercept yielding the concentration of ion present. The Orion Gran's Plot Paper now available[47] is a semi-antilog paper corrected for limited volume changes. Further reports on total concentration measurement are expected, particularly since Gran plots facilitate measurement on samples in which the level of the ion being determined is close to the electrode's limit of detection.[47] For the known-addition Gran plots, the top of the vertical (antilog) axis is equated to the potential of the electrode immersed in a solution containing 10 ml of known-addition solution plus 100 ml of test solution.

An early suggestion[46] for the application of Gran's method to the known-addition procedure is rather more cumbersome, for it involves calculation of

$$(V_0 + V)10^{-EF/2\cdot 303RT}$$

where E is the electrode response and V_0 and V are the volumes of the sample and known-addition solutions respectively.

Orion Gran's Plot Paper can also be used for the known-subtraction methods,[46] when the approach corresponds to a titration procedure. The known-subtraction method depends on a lowering of the activity of the uncomplexed ions by addition of a complexing agent, and the additional assumption that the complexing (or precipitating) agent is much stronger in its effect than any other present in the original sample. Calculations along similar lines to the known-addition method give the expression

$$E_2 - E_1 = \Delta E = \pm S \log \left(\frac{C_0 - C_\Delta}{C_0}\right) \tag{13}$$

Extensive computer tables of appropriate C_Δ and ΔE values are available to overcome the tedious arithmetic of the known-addition and known-subtraction calculations.[44]

Methods of coping with problems of wide variation of ionic strengths, interferents and complexing agents are not restricted to those above; further developments for dealing with special situations have been suggested and more can be expected. The use of a 1:1 dilution of both samples and standards with Total Ionic Strength Adjuster Buffer (TISAB) is an elegant example of a rapid method in fluoride determination for overcoming variations in ionic strength and possible presence of complexing cations such as iron(III) and aluminium(III).[49] The essential point is that the methods proposed should be as simple as possible and there should be adequate testing of the precision, reproducibility and recoveries under optimum conditions, including calculation of standard deviations and confidence limits.

Of course, subsequent experimentation can lead to suspicions of defectiveness, as has happened with TISAB interference[50,51] in the potentiometric titration of fluoride with lanthanum nitrate. Such interference has been attributed[50] to the carboxylate ion content of TISAB, and although the acetate is retained, citrate has now been replaced by DCTA (1,2-diaminocyclohexane,*N*,*N*,*N*′,*N*′-tetra-acetic acid) when analytical samples contain aluminium or iron.[52] However, for the direct determination of fluoride, the lanthanum fluoride electrode is only minimally affected by these carboxylate ions.[22]

Selective ion-sensitive electrodes in process control

Process control imposes additional demands and restrictions on the application of selective ion-sensitive electrodes. Direct monitoring of the process stream without supplementary chemistry is the simplest, but even here there must be adequate assessment of recalibration demands and of the severe limitations often imposed by leaching effects on the membrane. The latter is particularly marked for liquid ion-exchanger electrodes, where owing to leaching of the solvent, the solute becomes concentrated on the surface of the membrane with resultant sharp increase in potential.[53]

A watch must be kept for the creation of open circuits by the trapping of air bubbles at electrode tips and for static charges resulting from fast-moving process streams rubbing against the plastic walling of electrodes. Since the electrode will probably have been assessed for its suitability for analysis of the process solution under static conditions, publications on continuous monitoring applications must pay attention to these matters as well as to constancy of flow-rate of the process sample stream and the reagent streams. The results ought to be confirmed by information derived from intermittent sampling.

Compensation can be made for temperature fluctuation, but where the process sample stream contains a steady level of primary ion the need for compensation can be avoided by filling the electrode with a solution of the same concentration of primary ion as in the sample stream.

Titration procedures with selective ion-sensitive electrodes

Potentiometric procedures are of limited accuracy for direct concentration determination. However, for sufficiently high concentrations potentiometric titration gives good accuracy, for the potentiometry no longer depends on the exact interpretation of small changes in voltage and is not restricted by the accuracy of the electrode response to changes in solution concentration. However, development of suitable potentiometric titration procedures has a whole variety of possible pitfalls. Thus, in addition to the often severe limitations imposed by interferences, restricted concentration/activity range and response times of the electrodes, there are also the chemical factors of suitability of reagents, relative rates of reactions and the effects of pH and various side-reactions.

The variety of titration procedures with selective ion-sensitive electrodes indicates that problems associated with response times are surmountable, for example, Hadjiioannou and Papastathopoulos[54] claim that the time needed for the EDTA titration of calcium and magnesium with a calcium electrode varies from a few seconds to a few minutes. Even so, the point of maximum rate of potential change does not coincide with the equivalence point, and the over-titration must be at least partly due to sluggish response. Clearly a detailed investigation is necessary for the successful application of selective ion-sensitive electrodes for potentiometric titration. Thus, the slope of the titration curve, the overall voltage change, the blank, all depend on sample composition, buffer used and such experimental conditions as titrant delivery rate and concentration, stirring rate, size of beaker, position of delivery tip and depth of electrode immersion.[54]

There is much to commend the approach of Whitfield and Leyendekkers[55] which makes an initial theoretical assessment and examines possible problems of locating the equivalence point on practical titration curves from the standpoint of both chemical and potentiometric considerations. In this way possible effects of factors such as interferences, ionic strength and limitations imposed by restrictions in electrode response after the end-point can be anticipated. The electrode response can restrict[56] the simple application of $\Delta E/\Delta V$ *vs.* V relationships for end-point location.

There are other ways besides derivative methods for selecting the end-point.[56,57,58] The obvious one is to take the mid-point of the "potential jump" section of the normal E vs. V titration curve. Independent estimates by several observers help to avoid bias in the location of this point, or a computer programme based on least squares may be used. Alternatively, especially for unsymmetrical titration curves, a Gran plot[48] can be used, *e.g.*, on Orion Gran's Plot Paper.[47]

The final procedure should be tested on a wide range of solution compositions and rigorously tested statistically. In general it is fundamental that the end-point and equivalence point be as close as possible. Ambiguities in locating the end-point are intolerable and corrections through blanks, particularly if these are variable, are also not recommended.

Many useful hints on theoretical and practical aspects of titration procedures, including precision and accuracy of potentiometric end-point determination, are contained in two recent publications.[58,59]

Differential potentiometry

Membrane electrode potentials are normally measured with respect to a reversible reference electrode, *e.g.*, a calomel or silver–silver chloride electrode. Measurements may equally well be made with reference to another membrane electrode and in order to overcome the limitations imposed by the excessively high impedance of two membrane electrodes, Brand and Rechnitz[60] have described a new instrument. This can be used with, say, two glass electrodes making up the electrochemical cell and it has been assessed for sodium ion determinations, using a cell composed of a pH (reference) electrode and a sodium glass (indicator) electrode. Differential potentiometric titrations using glass reference and appropriate indicator electrodes are also discussed for calcium and copper determination by EDTA titration, but the assessment can only be described as incomplete because in view of the comments above on the coincidence of end-points with equivalence points of titration curves, the conclusion that the "shape of the titration curve was entirely adequate for analytical purposes" is insufficient. However, the paper[60] does show the prospective scope for widescale use of membrane electrodes as references for both direct potentiometry and potentiometric titration. Certain of the low impedance membrane electrodes, such as the fluoride electrodes have already been used[61,62] for these purposes.

CONCLUSIONS

The possible number of combinations of available selective ion-sensitive membrane electrodes and solution systems is already large and likely to increase considerably. Hence, because of the limitations due to interferences, complex formation and a whole variety of operating conditions, it is imperative that prospective users should be well-guided to make intelligent decisions regarding the advantages and limitations of a new electrode or application in the context of their own particular problem.

The following summary specifies a number of vital points to be included in reports on new electrodes and their applications. Emphasis is placed on realistic assessment in terms of speed, accuracy, cost, selectivity, simplicity, and comparison with other methods.

1. *A new or modified electrode.* In addition to constructional details and cell assembly, the report on the electrode must show assessments of useful activity/concentration range, response times and selectivity for the primary ion over other ions likely to be present in possible applications. Information on operational lifetime, freedom from drift and effective pH range at various activity levels should also be given.

2. *Applications for direct concentration/activity measurement.* Details must be given of the cell assembly, particularly of the reference electrode used with the selective ion-sensitive electrode. After information has been given on selectivity factors and means of overcoming interferences, the experimental procedure should be detailed, and this must avoid the addition of interferents. The activity/concentration values obtained must, whenever possible, be carefully compared with those given by traditional and established methods (if they exist). It is desirable that statistical tests of comparison be made and attention given to recoveries.

3. *On-line process applications.* The utility of any analytical system depends on accuracy and an on-line continuous pH monitoring system is considered good if it measures to ±0·02 pH unit representing a deviation of about ±1·2 mV at 25° or an error of about ±5% in the hydrogen activity measurement. Selective ion-sensitive electrodes have similar capabilities, but reports of applications to on-line continuous monitoring systems should clearly define the electrode behaviour as in 2 above and ought to include an assessment for intermittent samples as well as for continuous monitoring. This will help to characterize possible errors due to the additional parameters imposed by the flowing system.

4. *Titration applications.* Reports must attend to points concerning electrode behaviour and comparisons with established procedures as in 2. Special attention must be given to correct end-point location, to possible interferences, and to damage to electrodes by titration solutions.

Zusammenfassung—Es wird eine Übersicht über Entwicklung, Ansprechverhalten, Selektivität und Anwendungen selektiv ionenfindlicher Elektroden gegeben. Bezüglich der Entwicklung und Anwendung von Elektroden werden Empfehlungen ausgesprochen; auch die Art und Weise, wie Ergebnisse publiziert werden sollten, wird angesprochen.

Résumé—On passe en revue les caractères concernant le développement, la réponse, la sélectivité et les applications des électrodes sélectives sensibles aux ions. On fait des recommandations concernant les recherches impliquant le développement et les applications d'électrodes et l'on porte attention sur la manière de présenter les données pour publication.

REFERENCES

1. M. Cremer, *Z. Biol.*, 1906, **47**, 562.
2. F. Haber and Z. Klemensiewicz, *Z. Physik. Chem.*, 1909, **67**, 385.
3. B. Lengyel and E. Blum, *Trans. Faraday Soc.*, 1934, **30**, 464.
4. H. J. C. Tendeloo, *Proc. Acad. Sci. Amsterdam*, 1935, **38**, 434.
5. I. M. Kolthoff and H. L. Sanders, *J. Am. Chem. Soc.*, 1937, **59**, 416.
6. E. Pungor and E. Holós-Rokosinyi, *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 63.
7. M. S. Frant and J. W. Ross, *Science*, 1966, **154**, 1553.
8. R. A. Durst (Editor), *Ion Selective Electrodes*, Special Publication 314, National Bureau of Standards, Washington, D.C., 1969.
9. G. J. Moody and J. D. R. Thomas, *Lab. Practice*, 1971, **20**, 307.
10. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1203.
11. G. J. Moody and J. D. R. Thomas, *Talanta*, 1971, **18**, 1251.
12. G. J. Moody, R. B. Oke and J. D. R. Thomas, *Analyst*, 1970, **95**, 910.
13. S. Lal and G. D. Christian, *Anal. Chim. Acta*, 1970, **52**, 41.
14. G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes*, Merrow, Watford, England, 1971.
15. J. W. Ross, *Science*, 1967, **156**, 1378.
16. I. H. Krull, C. A. Mask and R. E. Cosgrove, *Anal. Letters*, 1970, **3**, 43.
17. T. S. Light and J. L. Swartz, *ibid.*, 1968, **1**, 825.
18. E. Pungor and K. Tóth, *Anal. Chim. Acta*, 1969, **47**, 291.
19. Orion Research Inc., *Newsletter*, 1969, **1**, 29.
20. K. Tóth and E. Pungor, *Proc. Intern. Measurement Confederation Symposium Electrochemical Sensors*, Veszprém, Hungary, 1968, 35.
21. Orion Research Inc., *Instruction Manual*, *Cyanide Activity Electrode*, Model 94-06.
22. P. A. Evans, G. J. Moody and J. D. R. Thomas, *Lab. Practice*, 1971, **20**, 644.
23. R. A. Durst and J. K. Taylor, *Anal. Chem.*, 1967, **39**, 1483.
24. J. J. Lingane, *ibid.*, 1967, **39**, 881.
25. K. Srinivasan and G. A. Rechnitz, *ibid.*, 1968, **40**, 509.
26. R. A. Durst, *ibid.*, 1969, **41**, 2089.
27. M. K. Mahendrappa, *Soil Science*, 1969, **108**, 132.
28. J. E. W. Davies, G. J. Moody and J. D. R. Thomas, *Analyst*, in the press.
29. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
30. G. A. Rechnitz, M. R. Kresz and S. B. Zamochnick, *Anal. Chem.*, 1966, **38**, 973.
31. G. A. Rechnitz and M. R. Kresz, *ibid.*, 1966, **38**, 1786.
32. T. M. Hseu and G. A. Rechnitz, *ibid.*, 1968, **40**, 1054.
33. G. A. Rechnitz and Z. F. Lin, *ibid.*, 1968, **40**, 696.
34. G. A. Rechnitz and T. M. Hseu, *ibid.*, 1969, **41**, 111.
35. E. Pungor and K. Tóth, *Analyst*, 1970, **95**, 625.
36. M. C. Gardels and J. C. Cornwell, *Anal. Chem.*, 1966, **38**, 774.
37. W. M. Wise, M. J. Kurey and G. Baum, *Clin. Chem.*, 1970, **16**, 103.
38. Orion Research Inc., *Newsletter*, 1969, **1**, 29.
39. B. F. Erlanger and R. A. Sack, *Anal. Biochem.*, 1970, **33**, 318.

40. A. Øien and A. R. Selmer-Olsen, *Analyst*, 1969, **94**, 888.
41. P. J. Milham, A. S. Awad, R. E. Paull and J. H. Bull, *ibid.*, 1970, **95**, 751.
42. J. I. Watters, S. Kalliney and R. C. Machen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3823.
43. Orion Research Inc., *Newsletter*, 1969, **1**, 5.
44. *Idem*, *ibid.*, 1969, **1**, 22.
45. *Idem*, *ibid.*, 1970, **2**, 5.
46. A. Liberti and M. Mascini, *Anal. Chem.*, 1969, **41**, 676.
47. Orion Research Inc., *Newsletter*, 1970, **2**, 49.
48. G. Gran, *Analyst*, 1952, **77**, 661.
49. M. S. Frant and J. W. Ross, *Anal. Chem.*, 1968, **40**, 1169.
50. T. Anfält and D. Jagner, *Anal. Chim. Acta*, 1969, **47**, 483.
51. *Idem*, *ibid.*, 1970, **50**, 23.
52. Orion Research Inc., *Applications Bulletin* No. 5A, 1969.
53. R. T. Oliver and R. F. Mannion, 16th National Symposium, Analysis Instrumentation Division, Instrument Society of America, Pittsburgh, Pennsylvania, May 25–27, 1970.
54. T. P. Hadjiioannou and D. S. Papastathopoulos, *Talanta*, 1970, **17**, 399.
55. M. Whitfield and J. V. Leyendekkers, *Anal. Chim. Acta*, 1969, **45**, 383.
56. M. Whitfield, J. V. Leyendekkers and J. D. Kerr, *ibid.*, 1969, **45**, 399.
57. T. Anfält, D. Dyrssen and D. Jagner, *ibid.*, 1968, **43**, 487.
58. T. Anfält and D. Jagner, *ibid.*, 1971, **57**, 165.
59. D. Jagner, *Abstracts of Gothenburg Dissertations in Science*, 1971, No. 25.
60. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1970, **42**, 616.
61. S. E. Manahan, *ibid.*, 1970, **42**, 128.
62. R. A. Durst, *ibid.*, 1968, **40**, 931.

Talanta, 1972, Vol. 19, pp. 623 to 639. Pergamon Press. Printed in Northern Ireland

DEVELOPMENT AND PUBLICATION OF WORK WITH SELECTIVE ION-SENSITIVE ELECTRODES

G. J. MOODY and J. D. R. THOMAS
University of Wales Institute of Science and Technology, Cardiff, Wales

(*Received* 7 *July* 1971)

Summary—Features concerning development, response, selectivity and applications of selective ion-sensitive electrodes are reviewed. Recommendations are made concerning investigations involving the development and applications of electrodes and attention given to the manner of presenting data for publication.

OVER SIXTY YEARS have elapsed since the initial discovery[1] and characterization[2] of the electrical potential arising at a thin glass membrane interposed between aqueous solutions of different acidity, but it is only within the last five or six years that there has been widespread development and interest in sensor membrane electrodes based upon a more general application of ion-exchanging materials. This might seem surprising when viewed against the prediction by Lengyel and Blum[3] in 1934 of a cation-sensitive glass electrode and of reports by Tendeloo[4] in 1935 and Kolthoff and Sanders[5] in 1937 detailing potentiometric response to certain ions by electrodes composed of solid-state membranes of barium sulphate and calcium fluoride slices[4] or discs of silver halides.[5]

Glass electrodes selective to hydrogen ions have been standard items of laboratory equipment for over thirty years, but it was just over ten years ago that glasses of modified composition were adapted for selective response to cations other than hydrogen ions. As the advantages of a wider range of selectively sensitive electrodes were materializing, Pungor and Holós-Rokosinyi[6] described in 1961 the selective working of precipitate-based ion-sensitive electrodes. However, it was the commercial availability of the fluoride solid-state electrode[7] in 1966, which coincided with the tremendous interest in the determination of trace fluoride following water fluoridation and dental health programmes, that initiated the recent vast interest in selective ion-sensitive electrodes. Symposia such as those held in January 1969 at the National Bureau of Standards, Gaithersburg, Maryland, U.S.A., and in February 1969 at the University of Wales Institute of Science and Technology, Cardiff, U.K., have boosted their general acceptance. The subsequent publication of the N.B.S. Symposium proceedings has provided a very useful source book[8] which has been well-supplemented by the Orion Research Incorporated Data Sheets and *Newsletter*.

The full benefit of selective ion-sensitive electrodes can only be realized by thorough familiarity with their properties and mode of operation. With this in view, this paper is intended to suggest a set of requirements in outlining the development, assessment and application of these electrodes. This is felt to be necessary in view of the existing ambiguities concerning the relation of potential to the logarithm of the activity of active ion and presentation of selectivity ratios or coefficients. Further reasons involve lifetimes and response time under various operating conditions. While it is recognized that different opinions and individual preferences will still flourish, it is nevertheless hoped that a format can be developed for the convenient presentation of results that will permit ease of assimilation and realistic appraisal by other workers.

DEVELOPMENT OF NEW ELECTRODES

Potential response

In general, the potentiometric cell assembly incorporating a selective ion-sensitive electrode takes the form shown in Fig. 1 where the e.m.f., E, of the cell is the sum of various junction potentials:

$$E = E_M + E_{M'} + E_R + E_{R'} + E_j \tag{1}$$

Except for E_M, which depends on the nature of the test or standardizing solution, the remaining contributory potentials may be taken as constant, although some of the junction potentials, particularly those of the reference electrode, can be troublesome. The reference electrode used in any investigation should be specified in published reports, along with the model and impedance of the e.m.f.-measuring instrument.

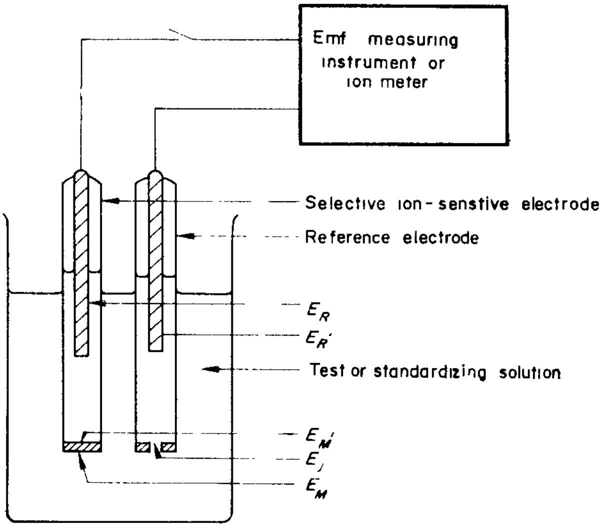


FIG. 1.—Experimental circuit for using selective ion-sensitive electrodes.

For an electrode responding selectively to an ion, i, of activity a_i and charge z, in the presence of an interfering ion, j, of activity a_j and charge y, E, for Nernstian response, is given by

$$E = \text{constant} \pm \frac{2{\cdot}303RT}{zF} \log [a_i + K_{ij}(a_j)^{z/y}] \tag{2}$$

where K_{ij} is the selectivity coefficient. The constant term incorporates the various junction potentials and the standard potential characteristic of E_M. The second term on the right-hand side of equation (2) takes the positive sign for cations and the negative for anions.

On the basis of the response characteristics above, selective ion-sensitive membrane electrodes have been described for about twenty ions which are fairly evenly divided between cations and anions. There is, therefore, plenty of scope for fresh developments, both for electrodes selectively sensitive to an extended range of ions and for improvements and refinements to existing electrodes.

Unless the electrode is going to be available commercially, its description should carry exact details for its construction, and the design need not be any more intricate than the minimum necessary for the performance claimed.

The dependence of the e.m.f. response on the logarithm of the activity indicates [equation (2) in the absence of interferent] that E will alter by only 2·72 mV for a univalent ion and by 1·36 mV for a bivalent ion for a 10% decrease in the activity of the active species and by only 2·45 mV for a univalent ion and by 1·23 mV for a bivalent ion for a 10% increase in the activity of the active species. These figures mean that a sensitive voltmeter (with high impedance to cope with the high resistances involved) responding to 0·1 mV, or better, is recommended[9] for work of acceptable precision. Expanded scale facilities on commercial pH-meters do not normally meet this requirement.

Selectivity

Membrane electrodes have the advantage that they can be tailor-made for almost any ion, but the difficulty of distinguishing adequately between different ions, particularly of the same sign, is a serious limitation. Hence, considerable effort has been devoted to assessing the performance of the new range of electrodes in the presence of possibly interfering ions. This has been done in terms of the selectivity coefficients, K_{ij}, defined by equation (2), the methods employed[9,10] for evaluating K_{ij} being based on e.m.f. measurements either in separate, or more realistically in mixed, solutions of the primary ion, i, and interfering ion, j.

The two separate-solution methods with the solutions producing e.m.f.s E_1 and E_2, involve either equation (3) or (4) depending, respectively, on equality of the primary and interferent ion activities and of the e.m.f.s:

$$\pm\left(\frac{E_2 - E_1}{2{\cdot}303RT/zF}\right) = \log K_{ij} + \left(\frac{z}{y} - 1\right)\log a_i \tag{3}$$

$$a_i = K_{ij}(a_j)^{z/y} \tag{4}$$

For cations, the left-hand side of equation (3) takes the positive sign, and the negative sign for anions. The second term of the right-hand side disappears when the charges of the primary and interfering ions are equal.

Separate solutions are not typical of operating systems so a more common procedure for assessing selectivity ratings is measurement of the e.m.f. in solutions containing a fixed amount of interferent with varying activities of the primary ion for which the electrode is designed. Figure 2 illustrates the general idealized pattern and the calculation of K_{ij} from equation (4).

It is pertinent at this point to stress the benefits[11] of the universal and consistent adoption of K_{ij} as described above for listing selectivity data. The inconsistencies to date, particularly in some manufacturers' literature, can only cause bewilderment to readers and users alike. Such a system of presenting selectivity data consistently indicates that when $K_{ij} < 1$ the electrode preferentially responds to the primary ion, i. However, Fig. 3 stresses the care needed in any interpretation of any single published item of selectivity information, for selectivity varies with the relative primary ion/interferent activities. Thus, for the poly(vinylchloride) calcium-sensitive electrode[12] the value $K_{\mathrm{CaMg}} = 0{\cdot}024$ obtained at a high magnesium content ($a_{\mathrm{Mg}} = 5 \times 10^{-3}M$)

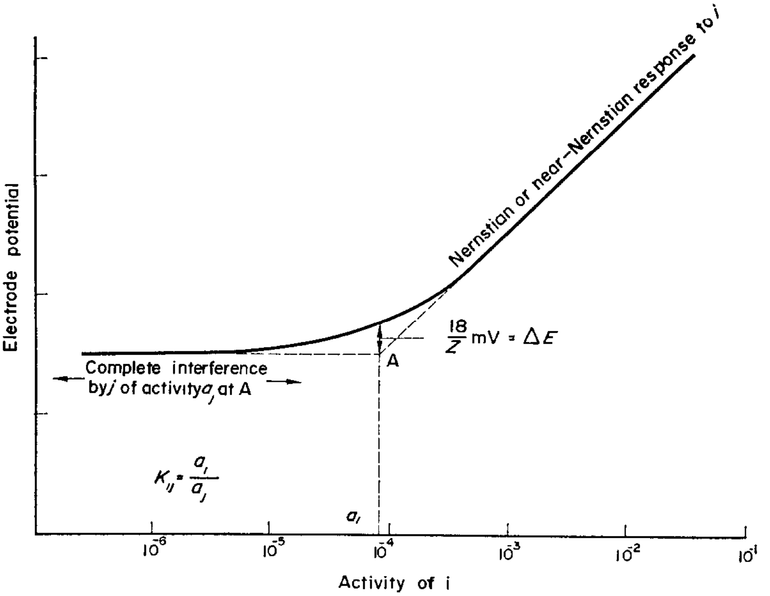


FIG. 2.—Illustration of selectivity coefficient evaluation, using fixed initial amount of interferent of same valence as *i*.

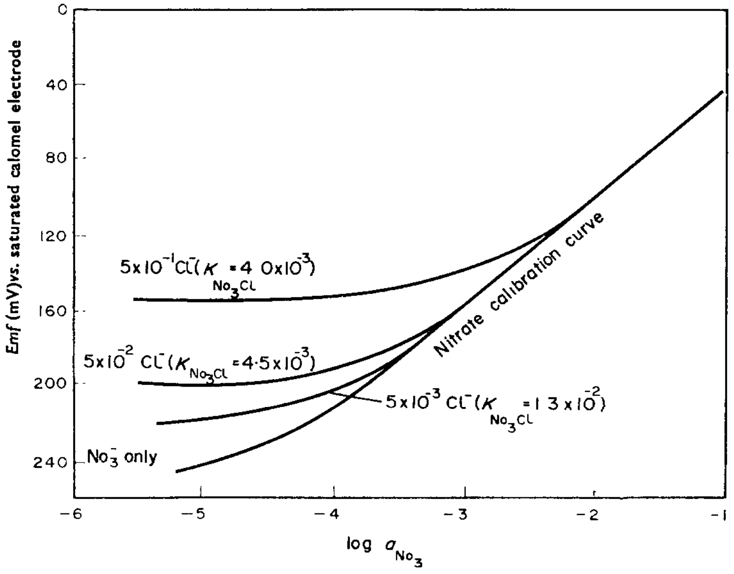


FIG. 3.—Influence of chloride on the response characteristics of a nitrate-sensitive (Orion 92-07-02 nitrate liquid ion exchanger) poly(vinylchloride) electrode.

suggests a better selectivity than $K_{CaMg} = 0{\cdot}222$ at a lower magnesium level ($a_{Mg} = 4{\cdot}3 \times 10^{-5}M$), while in fact the electrode gives the most extensively useful response at lower magnesium levels (*cf.* Fig. 3 for a nitrate-sensitive electrode affected by chloride interference).

The considerable variation of selectivity with interferent concentration is further illustrated by the work of Lal and Christian[13] on fifteen foreign cations, using the Orion 92–82 lead electrode. However, the apparent lack of critical assessment in this paper[13] emphasises the attention to detail essential for studies on electrode assessment. Thus, in commenting that the Orion lead electrode is much more responsive to univalent cations than is reported by the manufacturers, Lal and Christian[13] have not considered the modifying influence of the power term of equation (4). Yet this equation shows that the lead electrode has nearly the same useful range in the presence of $10^{-5}M$ sodium (down to $8{\cdot}9 \times 10^{-4}M$ lead) as it has in the presence of $10^{-5}M$ calcium (down to $2{\cdot}5 \times 10^{-4}M$ lead) even though the respective K_{ij} values differ by several orders of magnitude ($K_{\text{PbNa}} = 8{\cdot}9 \times 10^6$ and $K_{\text{PbCa}} = 25$). The extensive useful range permits the lead potentiometric titrations mentioned by these workers[13] but a high response to the sodium and potassium salt titrants used would hardly permit such an application. Moreover, potentiometric titrations of various univalent cations with sodium tetraphenylborate, with the lead electrode as sensor, warrant further investigation to determine the true mechanism.

The importance of the useful role of plots such as Fig. 3 for investigations involving interference parameters cannot be over-emphasized. Unfortunately, however, such plots take up journal space and where the mixed-solution method[9,10,13] has been employed, an alternative procedure[11] is to quote the activity, a_j, of the interfering ion corresponding to each K_{ij} value. Readers will then be realistically informed that should the level of j in the test situation exceed this value and the expected activity level of i be less than $K_{ij}(a_j)^{z/v}$, then the electrode will very likely be useless in such a test situation.

An alternative mixed-solution method of expressing selectivity involves variation of interferent activity at constant primary ion activity[9,10,14] and is generally used for assessing hydrogen ion and hydroxide ion interference. Several diagrams expressing constancy of e.m.f. response over a pH range have been published[12,15,16] and these confirm that unless there are unusual features it is adequate to quote a pH range for which there is unlikely to be interference with electrode behaviour, but again it is essential to quote the level of primary ion for that pH range.

Srinivasan and Rechnitz[10] considered neither of the foregoing mixed-solution methods in their treatment of potential data obtained for several different Orion liquid membrane ion-sensitive electrodes. Instead, two rather complicated equations were proposed, the general form of the one for high values of K_{ij} being

$$\left[\exp \pm \left(\frac{E_2 - E_1}{RT/zF}\right)\right] a_i - a_i' = K_{ij}(a_j')^{z/v} \tag{5}$$

and that for low values of K_{ij} being

$$a_i' - \left[\exp \pm \left(\frac{E_2 - E_1}{RT/zF}\right)\right] a_i = K_{ij}\left[\exp \pm \left(\frac{E_2 - E_1}{RT/zF}\right)(a_j)^{z/v} - (a_j')^{z/v}\right] \tag{6}$$

As before, the positive sign alternative is used for cation-sensitive electrodes and the negative for anion-sensitive electrodes. The a values refer to E_1, the a' values to E_2.

Equation (5) is used by plotting the left-hand side against interferent activities, a_j', and equation (6) is used by plotting the left-hand side against the square-bracketed function of the right-hand side. In each case, linear plots are obtained, of slope K_{ij}.

However, there is little to commend such complicated functions when the desired information concerning the potential applicability of electrodes can so conveniently be obtained from plots of the kind shown in Fig. 3.

Selectivities of solid-state electrodes have been variously expressed and emphasize the present chaos regarding selectivity quotations.[11,14] Except for the method involving equations (5) and (6), the practical methods employed for evaluating the selectivities are those already described above, although Light and Swartz[17] used equation (5) in a non-graphical procedure for determining anion interferences for the Orion 94-16 sulphide electrode.

The interference mechanism of solid-state electrodes differs from that of liquid ion-exchange and glass electrodes in the manner in which the primary ion and interfering ion(s) gain access to the all-important membrane.[14] This has led to criticism by Pungor and Tóth[18] concerning the application of the methods above for determining the selectivities of precipitate-based selective ion-sensitive electrodes. Even so, these workers used equation (4) in its appropriate form for obtaining "measured" selectivities of halide electrodes for comparison with those calculated from solubility product ratios.[18] This, of course, highlights a common form of interference of crystal membrane and precipitate-impregnated membrane electrodes, arising from the interfering ion actually reacting at the membrane surface to form a new insoluble compound.[19] For this kind of interference, a knowledge of solubility products of the membrane salt and of the insoluble compound formed is helpful in predicting the usefulness of an electrode. For example, for thiocyanate interference with the silver bromide electrode, the selectivity ratio, K_{BrSCN}, is given by the ratio of the solubility product of silver bromide to the solubility product of silver thiocyanate. This implies that for the electrode to be functional to bromide in the presence of thiocyanate, the ratio of the interfering thiocyanate to the primary bromide activity must not exceed the ratio (solubility product of AgSCN)/(solubility product of AgBr). Of course, the inverse relationship holds when the electrode is to be used for thiocyanate, with bromide interference, the form[11] of the selectivity ratio then being K_{SCNBr}.

Interference with solid-state electrodes also occurs when the membrane material reacts with interferent to give a soluble complex, a feature that has been exploited in adapting silver halide membranes for use as cyanide electrodes.[18,20,21] Dissolution of the membrane is also regarded as the basis of the "high" fluoride readings[14,22] obtained with the lanthanum fluoride electrode in the presence of citrate in dilute fluoride solutions.

Activity and ionic strength

The various equations for calculating selectivity coefficients depend upon a knowledge of activities and it follows that consistency and exact reporting of selectivity data ought also to include outline information on the calculation of the activity coefficient, f, which is used to calculate activity from concentration. Such information is especially desirable since the Debye-Hückel equation,

$$\log f = -Az^2\sqrt{\mu} \tag{7}$$

where A is a constant which for water is 0·511 at 25°, holds strictly only for zero ionic strength, μ, and its predictions differ from the behaviour of real electrolytes at ionic strengths greater than 10^{-3}–$10^{-2}M$. To meet this situation a variety of more or less empirical extensions to equation (7) have been proposed to fit the data (with varying success) at moderate values of ionic strength (Fig. 4).

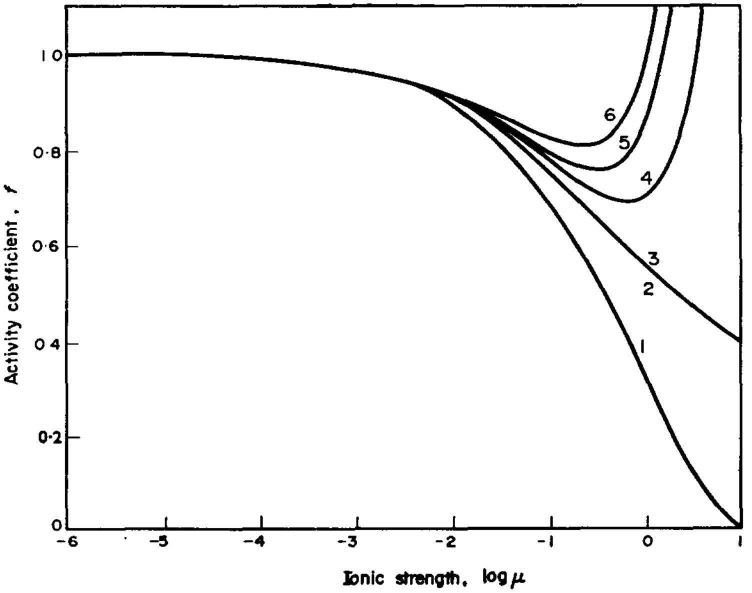


FIG. 4.—Computer simulations of various activity coefficient-ionic strength equations for univalent ions.

1. $\text{Log} f = -Az^2\sqrt{\mu}$
2. $\text{Log} f = \dfrac{-Az^2\sqrt{\mu}}{(1 + \sqrt{\mu})}$
3. $\text{Log} f = \dfrac{-Az^2\sqrt{\mu}}{(1 + 0{\cdot}329R\sqrt{\mu})}$ (R taken as 3 Å)
4. $\text{Log} f = -Az^2\left[\dfrac{\sqrt{\mu}}{1 + 1{\cdot}5\sqrt{\mu}} - 0{\cdot}2\,\mu\right]$
5. $\text{Log} f = -z^2\left[\dfrac{A\sqrt{\mu}}{1 + \sqrt{\mu}} - 0{\cdot}2\,\mu\right]$
6. $\text{Log} f = -z^2\left[\dfrac{A\sqrt{\mu}}{1 + 1{\cdot}5\sqrt{\mu}} - 0{\cdot}2\,\mu\right]$

The variation of the Debye-Hückel equation shown in equation (8) is extensively used in selective ion-sensitive electrode work for calculating the single ion activity:

$$\log f = -\frac{Az^2\sqrt{\mu}}{(1 + \sqrt{\mu})} \tag{8}$$

The ionic strength, μ, is given by

$$\mu = \tfrac{1}{2}\sum cz^2 \tag{9}$$

where c and z are the concentration and charge respectively of each ionic species present.

Stability of response

Closely related to selective response in the rating of ion-sensitive electrodes is drift and response time. Reports on steadiness and reproducibility of electrode response can provide useful guides to prospective users on frequency of recalibration and the suitability of the electrode for continuous process use.

Electrodes of different types are liable to different extents of drift, although wider drifts necessitating frequent recalibration can be tolerated when alternative methods of analysis are cumbersome or non-existent. Some electrodes have very low drift, *e.g.*, a potassium electrode with biological membrane (Beckman Catalogue No. 39622) for which daily checking during a continuous ten-day soaking period in $10^{-2}M$ potassium chloride "did not produce a noticeable drift."[16] However, an accompanying table does show differences in response of up to ±2 mV after ten days, compared with the initial response.[16] No results are quoted for the intervening period, although the ten-day results cover the potassium concentration range 10^{-5}–$10^{-1}M$ ($9{\cdot}96 \times 10^{-6}$–$7{\cdot}7 \times 10^{-2}M$ activity).

Data[22–24] for the well-established and widely used lanthanum fluoride crystal membrane fluoride-responsive electrode indicate a similar ±2 mV drift for the Orion 94-09 model, although Srinivasan and Rechnitz[25] report drifts of up to 7 mV depending on stirring and activity conditions, the response being steadier at high ionic strengths.

Miniaturization of electrodes is desirable for *in vivo* measurements or for *in situ* studies where solution volume is a limitation.[26] However, design demands can lead to specification change and for this reason reports should clearly specify electrode types used. Thus, for a fluoride microelectrode[26] the zero potential varied by about ±20 mV from day to day but, on the other hand, depth of immersion had little effect on the potential, the e.m.f. shift being about −2 mV over the 1 mm length of the exposed lanthanum fluoride crystal.

While 2 mV drifts may seem insignificant, it must be emphasized that drifts of this magnitude can lead to errors of several per cent. Frequent recalibration of selective ion-sensitive membrane electrodes is therefore essential, especially for the liquid ion-exchanger membrane electrodes which are reported to have drifts of over 2 mV for a single day's use,[12,27,28] even extending to 70 mV for an Orion 92-07 nitrate electrode.[27] However, provided the calibration slope does not alter with time, recalibration is a simple matter and not a serious drawback, particularly when alternative analysis procedures are cumbersome or non-existent.

Calibration slopes

Equation (2) suggests that calibration slopes should be $59/z$ mV at 25°. For selective ion-sensitive electrodes this is far from universally true, although slopes are normally within 2–3 mV of the Nernstian value. This is no inconvenience so long as the particular calibration slope does not change with time, and unlike the overall drifts mentioned above, slopes have been found to be extremely steady during normal electrode life; if not, failure of the electrode is indicated.

A drastic change in slope can often be related to some malfunction of the reference electrode, whereas failure of a functional selective-ion sensitive electrode is more gradual, being manifested as a drop in calibration slope.

As with drifts, some very large deviations in calibration slope have been reported;

for example, slopes ranging from 64 to 50 mV per activity decade and attributed to defective assembly have been reported[27] for the liquid ion-exchanger Orion 92-07 nitrate electrode.

Deviations from Nernstian behaviour may be attributed to incomplete permselectivity of the membrane, a factor which Helfferich[29] covered by an integral term in the function for membrane potential to account for the co-ion flux. Such integrals may be evaluated graphically, but this is of no benefit in the present context and for general application here it is adequate to take a coefficient, S, instead of $2{\cdot}303RT/zF$ in equation (2), where S is the calibration slope.

Speed of response

Several studies have been made of the response times of selective ion-sensitive electrodes, principally by Rechnitz[30–34] and Pungor,[35] although descriptions of new electrodes frequently include details of response times.[12,16,28] In general, liquid exchanger ion-sensitive membrane electrodes respond less rapidly than the solid-state type.

It can be argued that rather too much emphasis has been placed on response times of electrodes; this is certainly the case for direct potentiometric determination of activity where response times of some minutes are quite tolerable. However, automatic analysers and continuous-measurement cells require sensors with more rapid response, and response times of minutes are too long for kinetic work and potentiometric titrations.

In attempts to determine very short response times, the relatively high time-constants of measuring instruments can be a limitation, but when electrodes with such ideal time responses have been achieved, there is no reason for obsession with this characteristic until the measuring instruments and the slow equilibration of junction potentials within the measuring-cell have been improved.

Response times are usually measured either by immersing the electrode in the solution and finding the time needed to reach equilibrium, or by injecting a solution of appropriate concentration into the system in which the electrode is already immersed. The equilibration can be monitored by chart-recorder, but Pungor[35] used an oscilloscope for times in the millisecond range. Response time data should be given for change from dilute to concentrated solution and for change in the opposite direction, and in addition, for reading within 1 mV of the equilibrium value. The latter times are usually a mere fraction of the full equilibration times and can provide guides for continuous monitoring and potentiometric applications. Indeed, where full equilibration times are long, the "1-mV times" can be short enough for rapid potentiometric titration rather than the intermittent start and stop of the burette system in automatic systems that is sometimes necessary[36] in order to allow equilibration near the equivalence point. However, there are few reports on response times in mixed solutions.

It is interesting that electrode response is very steady during stirring[12,16,25,33,34] and that base-line noise levels of recorders are only important at low activities.[16] However, there can be differences in potential response between stirred and unstirred solutions[25] and for different rates of stirring.[33,34] Differences of 0·4 and 6 mV have been observed[25] in the potential response of the Orion 94-09 fluoride electrode for

10^{-1} and $10^{-3}M$ fluoride solutions respectively, although at high ionic strengths, for example in $1M$ sodium nitrate, no such differences are evident.[25]

Conditioning and storage of electrodes

As with glass electrodes, the selective ion-sensitive electrodes often need conditioning before use. The description of any new electrode should specify any conditioning needed, particularly when there are unusual features such as the need to age the Corning Model No. 476132 potassium electrode in a solution having a composition simulating that of the test solution in order to avoid long response times and hysteresis effects.[37] Similarly, information should be given on the conditioning necessary to recover from detrimental circumstances; for example, liquid ion-exchanger calcium electrodes take an hour to regain proper response potentials to pure calcium chloride solutions after exposure to zinc chloride[12] and, after exposure to perchlorate, nitrate electrodes take almost as long to return to normal behaviour.[28] Silver thiocyanate should be removed from the membrane (by wiping or with a toothbrush and toothpaste) of silver bromide electrodes after exposure to interfering levels of thiocyanate.[38]

Storage conditions for electrodes when not in use should also be stated.

APPLICATION OF SELECTIVE ION-SENSITIVE ELECTRODES

The recent interest in selective ion-sensitive electrodes has resulted in about 400 papers devoted to development and uses. A large proportion concern the specification and appraisal of electrodes, but as the rate of appearance of new electrodes might be expected to diminish, it can be expected that an increasing proportion of future publications will be devoted to application and mechanism.

It is therefore necessary to specify which factors must be examined in development of an application, and what information must be given in any paper published on the work done.

The applications are generally to direct determination of activity (or concentration), or to titration procedures.

With adequate attention to calibration, particularly at low concentration levels and low ionic strength, selective ion-sensitive electrodes may be used for direct concentration measurements.

In using membrane electrodes, precautions must therefore be taken against complications at high concentrations and due to other ionic species with respect to variation of activity with ionic strength. Interference effects must also be tested at realistic levels. For example, bearing in mind equation (4), there is *no* point in attempting to use a nitrate electrode with selectivity coefficient $K_{NO_3Cl} = 4 \times 10^{-3}$ determined for a chloride level of $0{\cdot}5M$, when assessing soil nitrate in concentrations of about $10^{-4}M$, when $2M$ potassium chloride is the extracting agent. This is evident from Fig. 3, which confirms that the response would be constant regardless of the nitrate activity. However, $0{\cdot}01M$ copper sulphate or water could be used as extractant,[40] although saline soils high in chloride might require supplementary treatment.

Both the Øien[40] and Milham[41] papers on soil nitrate determination are thorough in their enquiry and can serve as models for this kind of publication, although the former tends to include ambiguous statements. Both give due attention to comparisons with established methods, recovery, a wide variety of samples, and the limitations of published selectivity coefficients and of making corrections by equations, which for complicated systems of this kind would demand selectivity terms additional to the single one given in equation (2). Hence, Milham *et al.*[41] used rather an involved buffer system to cope with some interferents: a low pH kept the equilibrium bicarbonate low and the water-extractable organic acids undissociated; aluminium was added to complex anions of organic acids, and sulphamic acid was used to destroy nitrite quantitatively.

Both papers also pay attention to possible effects of ionic strength, and give information on electrode conditioning and mixing times before measurement. The inclusion of the correlation coefficient and regression equation is also valuable.

Concentration measurements of uncomplexed ions

Exhaustive examination of the effect of ionic strength is necessary for appraisal of the application of selective ion-sensitive electrodes. Conductance monitoring may not give satisfactory guidance—possibly because of the power term in z in equation (9). Though direct measurement on the sample can give acceptable results, it is only when a sample consists largely of one salt that an activity–e.m.f. calibration plot can be used accurately. However, such a plot may be acceptable for mixed solutions if the ratio of the primary ion to that of the other ions is constant. For example, to estimate potassium in sea-water, calibration standards are made by diluting synthetic potassium sea-water samples with demineralized water.[14]

The constant ionic-background method is frequently used when the analytical sample contains a high but essentially constant level of ions besides the one of interest. Calibration standards of similar composition are then employed, but ions at interfering levels must be absent, of course.

If samples exhibit considerable overall variation in composition, adding an "ionic strength adjuster" to the sample and calibration solutions tends to bring all the solutions to a common ionic strength. It is assumed that the ultimate ionic strength arises almost exclusively from the ionic strength adjuster and not the sample itself. This is the basis of the involved buffer system[41] described above for nitrate determination in various materials, although the buffer was also a judicious recipe to meet the selectivity parameters of the electrode. Though virtually any substance may serve as an ionic strength adjuster, it must not complex with the primary ion, and the selectivity coefficient, K_{ij}, where j is the ionic strength adjuster, must be negligible. Tetramethylammonium nitrate was chosen for this reason for an investigation[42] of calcium complexes with tri- and tetrametaphosphate, using a calcium-selective liquid ion-exchange membrane electrode. Certain variations may sometimes be necessary in addition to ionic strength adjustment, for example, pH adjustment will release anions of weak acids. Thus, at pH 10·5 the cyanide ion is present and not undissociated hydrocyanic acid.[35]

Measurements of total concentration

The methods just discussed give the concentrations (or activities) of free (that is, uncomplexed) ions. These may be quite different from the total concentrations (that is, free + complexed species). Two elegant methods are now available for total concentration measurements.[43,44,45] Electrode calibration is not usually necessary and only two potentials need be taken.

Both methods require a change in the concentration of the primary ion, *i*. For *known addition* (otherwise known as the *spiking* or *known-increment method*) more *i* is introduced, whereas in *known subtraction* the level of *i* is lowered by adding a complexing agent. There are no complications from ionic strengths as in the previous cases.

In the known-addition method, the potential, E_1, is measured for the sample solution of volume V_0 and total molar concentration C_0 of species sought,

$$E_1 = \text{constant} \pm S \log x_1 f_1 C_0 \tag{10}$$

where S is the electrode calibration slope, f_1 is the activity coefficient and x_1 the mole fraction of uncomplexed ions. A new potential, E_2, is then measured after addition of a small volume, V_A, of a standard solution (concentration C_s) of ions of the species sought where $C_s \sim 100C_0$:

$$E_2 = \text{constant} \pm S \log (x_2 f_2 C_0 + x_2 f_2 C_\Delta) \tag{11}$$

where f_2 and x_2 correspond to the new activity coefficient and mole fraction of free ions, respectively, and C_Δ is the change in concentration, given by $V_A C_s / V_0$. An essential assumption is that $x_1 \sim x_2$ and $f_1 \sim f_2$. Hence the difference between equations (10) and (11) simplifies to

$$E_2 - E_1 = \Delta E = \pm S \log \left(\frac{C_0 + C_\Delta}{C_0} \right) \tag{12}$$

and C_0 can be calculated.

A variation of the known addition method has recently been recommended[46,47] and is based on a modification of the method described by Gran[48] for presenting potentiometric titration data in linear form by using a semi-antilog plot. The method[47] involves plotting the appropriate potential response on the vertical antilog axis against volume (ml) of "known addition" with the intercept yielding the concentration of ion present. The Orion Gran's Plot Paper now available[47] is a semi-antilog paper corrected for limited volume changes. Further reports on total concentration measurement are expected, particularly since Gran plots facilitate measurement on samples in which the level of the ion being determined is close to the electrode's limit of detection.[47] For the known-addition Gran plots, the top of the vertical (antilog) axis is equated to the potential of the electrode immersed in a solution containing 10 ml of known-addition solution plus 100 ml of test solution.

An early suggestion[46] for the application of Gran's method to the known-addition procedure is rather more cumbersome, for it involves calculation of

$$(V_0 + V)10^{-EF/2\cdot 303RT}$$

where E is the electrode response and V_0 and V are the volumes of the sample and known-addition solutions respectively.

Orion Gran's Plot Paper can also be used for the known-subtraction methods,[46] when the approach corresponds to a titration procedure. The known-subtraction method depends on a lowering of the activity of the uncomplexed ions by addition of a complexing agent, and the additional assumption that the complexing (or precipitating) agent is much stronger in its effect than any other present in the original sample. Calculations along similar lines to the known-addition method give the expression

$$E_2 - E_1 = \Delta E = \pm S \log \left(\frac{C_0 - C_\Delta}{C_0} \right) \tag{13}$$

Extensive computer tables of appropriate C_Δ and ΔE values are available to overcome the tedious arithmetic of the known-addition and known-subtraction calculations.[44]

Methods of coping with problems of wide variation of ionic strengths, interferents and complexing agents are not restricted to those above; further developments for dealing with special situations have been suggested and more can be expected. The use of a 1 :1 dilution of both samples and standards with Total Ionic Strength Adjuster Buffer (TISAB) is an elegant example of a rapid method in fluoride determination for overcoming variations in ionic strength and possible presence of complexing cations such as iron(III) and aluminium(III).[49] The essential point is that the methods proposed should be as simple as possible and there should be adequate testing of the precision, reproducibility and recoveries under optimum conditions, including calculation of standard deviations and confidence limits.

Of course, subsequent experimentation can lead to suspicions of defectiveness, as has happened with TISAB interference[50,51] in the potentiometric titration of fluoride with lanthanum nitrate. Such interference has been attributed[50] to the carboxylate ion content of TISAB, and although the acetate is retained, citrate has now been replaced by DCTA (1,2-diaminocyclohexane,*N*,*N*,*N'*,*N'*-tetra-acetic acid) when analytical samples contain aluminium or iron.[52] However, for the direct determination of fluoride, the lanthanum fluoride electrode is only minimally affected by these carboxylate ions.[22]

Selective ion-sensitive electrodes in process control

Process control imposes additional demands and restrictions on the application of selective ion-sensitive electrodes. Direct monitoring of the process stream without supplementary chemistry is the simplest, but even here there must be adequate assessment of recalibration demands and of the severe limitations often imposed by leaching effects on the membrane. The latter is particularly marked for liquid ion-exchanger electrodes, where owing to leaching of the solvent, the solute becomes concentrated on the surface of the membrane with resultant sharp increase in potential.[53]

A watch must be kept for the creation of open circuits by the trapping of air bubbles at electrode tips and for static charges resulting from fast-moving process streams rubbing against the plastic walling of electrodes. Since the electrode will probably have been assessed for its suitability for analysis of the process solution under static conditions, publications on continuous monitoring applications must pay attention to these matters as well as to constancy of flow-rate of the process sample stream and the reagent streams. The results ought to be confirmed by information derived from intermittent sampling.

Compensation can be made for temperature fluctuation, but where the process sample stream contains a steady level of primary ion the need for compensation can be avoided by filling the electrode with a solution of the same concentration of primary ion as in the sample stream.

Titration procedures with selective ion-sensitive electrodes

Potentiometric procedures are of limited accuracy for direct concentration determination. However, for sufficiently high concentrations potentiometric titration gives good accuracy, for the potentiometry no longer depends on the exact interpretation of small changes in voltage and is not restricted by the accuracy of the electrode response to changes in solution concentration. However, development of suitable potentiometric titration procedures has a whole variety of possible pitfalls. Thus, in addition to the often severe limitations imposed by interferences, restricted concentration/activity range and response times of the electrodes, there are also the chemical factors of suitability of reagents, relative rates of reactions and the effects of pH and various side-reactions.

The variety of titration procedures with selective ion-sensitive electrodes indicates that problems associated with response times are surmountable, for example, Hadjiioannou and Papastathopoulos[54] claim that the time needed for the EDTA titration of calcium and magnesium with a calcium electrode varies from a few seconds to a few minutes. Even so, the point of maximum rate of potential change does not coincide with the equivalence point, and the over-titration must be at least partly due to sluggish response. Clearly a detailed investigation is necessary for the successful application of selective ion-sensitive electrodes for potentiometric titration. Thus, the slope of the titration curve, the overall voltage change, the blank, all depend on sample composition, buffer used and such experimental conditions as titrant delivery rate and concentration, stirring rate, size of beaker, position of delivery tip and depth of electrode immersion.[54]

There is much to commend the approach of Whitfield and Leyendekkers[55] which makes an initial theoretical assessment and examines possible problems of locating the equivalence point on practical titration curves from the standpoint of both chemical and potentiometric considerations. In this way possible effects of factors such as interferences, ionic strength and limitations imposed by restrictions in electrode response after the end-point can be anticipated. The electrode response can restrict[56] the simple application of $\Delta E/\Delta V$ *vs.* V relationships for end-point location.

There are other ways besides derivative methods for selecting the end-point.[56,57,58] The obvious one is to take the mid-point of the "potential jump" section of the normal E vs. V titration curve. Independent estimates by several observers help to avoid bias in the location of this point, or a computer programme based on least squares may be used. Alternatively, especially for unsymmetrical titration curves, a Gran plot[48] can be used, *e.g.*, on Orion Gran's Plot Paper.[47]

The final procedure should be tested on a wide range of solution compositions and rigorously tested statistically. In general it is fundamental that the end-point and equivalence point be as close as possible. Ambiguities in locating the end-point are intolerable and corrections through blanks, particularly if these are variable, are also not recommended.

Many useful hints on theoretical and practical aspects of titration procedures, including precision and accuracy of potentiometric end-point determination, are contained in two recent publications.[58,59]

Differential potentiometry

Membrane electrode potentials are normally measured with respect to a reversible reference electrode, *e.g.*, a calomel or silver–silver chloride electrode. Measurements may equally well be made with reference to another membrane electrode and in order to overcome the limitations imposed by the excessively high impedance of two membrane electrodes, Brand and Rechnitz[60] have described a new instrument. This can be used with, say, two glass electrodes making up the electrochemical cell and it has been assessed for sodium ion determinations, using a cell composed of a pH (reference) electrode and a sodium glass (indicator) electrode. Differential potentiometric titrations using glass reference and appropriate indicator electrodes are also discussed for calcium and copper determination by EDTA titration, but the assessment can only be described as incomplete because in view of the comments above on the coincidence of end-points with equivalence points of titration curves, the conclusion that the "shape of the titration curve was entirely adequate for analytical purposes" is insufficient. However, the paper[60] does show the prospective scope for widescale use of membrane electrodes as references for both direct potentiometry and potentiometric titration. Certain of the low impedance membrane electrodes, such as the fluoride electrodes have already been used[61,62] for these purposes.

CONCLUSIONS

The possible number of combinations of available selective ion-sensitive membrane electrodes and solution systems is already large and likely to increase considerably. Hence, because of the limitations due to interferences, complex formation and a whole variety of operating conditions, it is imperative that prospective users should be well-guided to make intelligent decisions regarding the advantages and limitations of a new electrode or application in the context of their own particular problem.

The following summary specifies a number of vital points to be included in reports on new electrodes and their applications. Emphasis is placed on realistic assessment in terms of speed, accuracy, cost, selectivity, simplicity, and comparison with other methods.

1. *A new or modified electrode.* In addition to constructional details and cell assembly, the report on the electrode must show assessments of useful activity/concentration range, response times and selectivity for the primary ion over other ions likely to be present in possible applications. Information on operational lifetime, freedom from drift and effective pH range at various activity levels should also be given.

2. *Applications for direct concentration/activity measurement.* Details must be given of the cell assembly, particularly of the reference electrode used with the selective ion-sensitive electrode. After information has been given on selectivity factors and means of overcoming interferences, the experimental procedure should be detailed, and this must avoid the addition of interferents. The activity/concentration values obtained must, whenever possible, be carefully compared with those given by traditional and established methods (if they exist). It is desirable that statistical tests of comparison be made and attention given to recoveries.

3. *On-line process applications.* The utility of any analytical system depends on accuracy and an on-line continuous pH monitoring system is considered good if it measures to ±0·02 pH unit representing a deviation of about ±1·2 mV at 25° or an error of about ±5% in the hydrogen activity measurement. Selective ion-sensitive electrodes have similar capabilities, but reports of applications to on-line continuous monitoring systems should clearly define the electrode behaviour as in 2 above and ought to include an assessment for intermittent samples as well as for continuous monitoring. This will help to characterize possible errors due to the additional parameters imposed by the flowing system.

4. *Titration applications.* Reports must attend to points concerning electrode behaviour and comparisons with established procedures as in 2. Special attention must be given to correct end-point location, to possible interferences, and to damage to electrodes by titration solutions.

Zusammenfassung—Es wird eine Übersicht über Entwicklung, Ansprechverhalten, Selektivität und Anwendungen selektiv ionenfindlicher Elektroden gegeben. Bezüglich der Entwicklung und Anwendung von Elektroden werden Empfehlungen ausgesprochen; auch die Art und Weise, wie Ergebnisse publiziert werden sollten, wird angesprochen.

Résumé—On passe en revue les caractères concernant le développement, la réponse, la sélectivité et les applications des électrodes sélectives sensibles aux ions. On fait des recommandations concernant les recherches impliquant le développement et les applications d'électrodes et l'on porte attention sur la manière de présenter les données pour publication.

REFERENCES

1. M. Cremer, *Z. Biol.*, 1906, **47**, 562.
2. F. Haber and Z. Klemensiewicz, *Z. Physik. Chem.*, 1909, **67**, 385.
3. B. Lengyel and E. Blum, *Trans. Faraday Soc.*, 1934, **30**, 464.
4. H. J. C. Tendeloo, *Proc. Acad. Sci. Amsterdam*, 1935, **38**, 434.
5. I. M. Kolthoff and H. L. Sanders, *J. Am. Chem. Soc.*, 1937, **59**, 416.
6. E. Pungor and E. Holós-Rokosinyi, *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 63.
7. M. S. Frant and J. W. Ross, *Science*, 1966, **154**, 1553.
8. R. A. Durst (Editor), *Ion Selective Electrodes*, Special Publication 314, National Bureau of Standards, Washington, D.C., 1969.
9. G. J. Moody and J. D. R. Thomas, *Lab. Practice*, 1971, **20**, 307.
10. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1203.
11. G. J. Moody and J. D. R. Thomas, *Talanta*, 1971, **18**, 1251.
12. G. J. Moody, R. B. Oke and J. D. R. Thomas, *Analyst*, 1970, **95**, 910.
13. S. Lal and G. D. Christian, *Anal. Chim. Acta*, 1970, **52**, 41.
14. G. J. Moody and J. D. R. Thomas, *Selective Ion-Sensitive Electrodes*, Merrow, Watford, England, 1971.
15. J. W. Ross, *Science*, 1967, **156**, 1378.
16. I. H. Krull, C. A. Mask and R. E. Cosgrove, *Anal. Letters*, 1970, **3**, 43.
17. T. S. Light and J. L. Swartz, *ibid.*, 1968, **1**, 825.
18. E. Pungor and K. Tóth, *Anal. Chim. Acta*, 1969, **47**, 291.
19. Orion Research Inc., *Newsletter*, 1969, **1**, 29.
20. K. Tóth and E. Pungor, *Proc. Intern. Measurement Confederation Symposium Electrochemical Sensors*, Veszprém, Hungary, 1968, 35.
21. Orion Research Inc., *Instruction Manual, Cyanide Activity Electrode*, Model 94-06.
22. P. A. Evans, G. J. Moody and J. D. R. Thomas, *Lab. Practice*, 1971, **20**, 644.
23. R. A. Durst and J. K. Taylor, *Anal. Chem.*, 1967, **39**, 1483.
24. J. J. Lingane, *ibid.*, 1967, **39**, 881.
25. K. Srinivasan and G. A. Rechnitz, *ibid.*, 1968, **40**, 509.
26. R. A. Durst, *ibid.*, 1969, **41**, 2089.
27. M. K. Mahendrappa, *Soil Science*, 1969, **108**, 132.
28. J. E. W. Davies, G. J. Moody and J. D. R. Thomas, *Analyst*, in the press.
29. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
30. G. A. Rechnitz, M. R. Kresz and S. B. Zamochnick, *Anal. Chem.*, 1966, **38**, 973.
31. G. A. Rechnitz and M. R. Kresz, *ibid.*, 1966, **38**, 1786.
32. T. M. Hseu and G. A. Rechnitz, *ibid.*, 1968, **40**, 1054.
33. G. A. Rechnitz and Z. F. Lin, *ibid.*, 1968, **40**, 696.
34. G. A. Rechnitz and T. M. Hseu, *ibid.*, 1969, **41**, 111.
35. E. Pungor and K. Tóth, *Analyst*, 1970, **95**, 625.
36. M. C. Gardels and J. C. Cornwell, *Anal. Chem.*, 1966, **38**, 774.
37. W. M. Wise, M. J. Kurey and G. Baum, *Clin. Chem.*, 1970, **16**, 103.
38. Orion Research Inc., *Newsletter*, 1969, **1**, 29.
39. B. F. Erlanger and R. A. Sack, *Anal. Biochem.*, 1970, **33**, 318.

40. A. Øien and A. R. Selmer-Olsen, *Analyst*, 1969, **94**, 888.
41. P. J. Milham, A. S. Awad, R. E. Paull and J. H. Bull, *ibid.*, 1970, **95**, 751.
42. J. I. Watters, S. Kalliney and R. C. Machen, *J. Inorg. Nucl. Chem.*, 1969, **31**, 3823.
43. Orion Research Inc., *Newsletter*, 1969, **1**, 5.
44. *Idem*, *ibid.*, 1969, **1**, 22.
45. *Idem*, *ibid.*, 1970, **2**, 5.
46. A. Liberti and M. Mascini, *Anal. Chem.*, 1969, **41**, 676.
47. Orion Research Inc., *Newsletter*, 1970, **2**, 49.
48. G. Gran, *Analyst*, 1952, **77**, 661.
49. M. S. Frant and J. W. Ross, *Anal. Chem.*, 1968, **40**, 1169.
50. T. Anfält and D. Jagner, *Anal. Chim. Acta*, 1969, **47**, 483.
51. *Idem*, *ibid.*, 1970, **50**, 23.
52. Orion Research Inc., *Applications Bulletin* No. 5A, 1969.
53. R. T. Oliver and R. F. Mannion, 16th National Symposium, Analysis Instrumentation Division, Instrument Society of America, Pittsburgh, Pennsylvania, May 25–27, 1970.
54. T. P. Hadjiioannou and D. S. Papastathopoulos, *Talanta*, 1970, **17**, 399.
55. M. Whitfield and J. V. Leyendekkers, *Anal. Chim. Acta*, 1969, **45**, 383.
56. M. Whitfield, J. V. Leyendekkers and J. D. Kerr, *ibid.*, 1969, **45**, 399.
57. T. Anfält, D. Dyrssen and D. Jagner, *ibid.*, 1968, **43**, 487.
58. T. Anfält and D. Jagner, *ibid.*, 1971, **57**, 165.
59. D. Jagner, *Abstracts of Gothenburg Dissertations in Science*, 1971, No. 25.
60. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1970, **42**, 616.
61. S. E. Manahan, *ibid.*, 1970, **42**, 128.
62. R. A. Durst, *ibid.*, 1968, **40**, 931.

Talanta, 1972, Vol. 19, pp. 641 to 645. Pergamon Press. Printed in Northern Ireland

IODOMETRIC MICRODETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS BY AN AMPLIFICATION REACTION

Y. A. GAWARGIOUS* and A. B. FARAG
Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, U.A.R.

(*Received* 31 *March* 1971. *Accepted* 8 *July* 1971)

Summary—A new method is described for the iodometric microdetermination of sulphur in organic compounds, using a 12-fold amplification reaction after oxygen-flask combustion. The method is based on reaction of the resulting sulphuric acid with an excess of saturated barium bromate solution. The unreacted barium bromate is precipitated by addition of acetone, filtered off, redissolved in hot water and after addition of an excess of iodide and acid, the iodine liberated is titrated with thiosulphate. The method is simple, rapid, highly accurate, and of wide application in the microanalysis of organosulphur compounds containing other common acid-forming elements.

SEVERAL methods are available in the literature for the determination of sulphur in organic compounds *via* sulphate estimation.[1–5] Redox titration methods after precipitation as barium sulphate, with slightly soluble salts such as barium iodate or chromate, were suggested by Andrews[6] and Sojbelman[7] and described in greater detail by Erdey and Banyai.[8] In a recent publication, Jaselskis and Vas[9] revived the barium iodate method for the semimicro determination of the sulphate ion in synthetic inorganic mixtures. They determined sulphate iodometrically, using a 3-hr equilibration of the sulphate solution with solid barium iodate in 40% acetone–$0{\cdot}1M$ aqueous acetic acid mixture. The liberated iodate was determined iodometrically after separation of the mixed precipitates of barium sulphate and barium iodate. Although an amplified iodometric reaction is involved, the procedure is time-consuming, and is not suitable for the microdetermination of sulphur in organic compounds.

Recently, Prokopov[10] published a method for the iodometric microdetermination of sulphur in organic compounds containing C, H, O, and S. The method is based upon combustion in the oxygen flask, with use of aqueous hydrogen peroxide as absorbant to convert sulphur combustion products into sulphuric acid. Addition of an excess of potassium iodide and iodate to the solution liberates iodine which is then titrated with thiosulphate. Unfortunately, this method cannot be used when other acid-forming elements are present in the organic compound. Various attempts[11] have been made to eliminate such interferences but the procedures tend to be rather lengthy and complicated and were thus ignored.

In the present investigation a new amplification method is described for the iodometric microdetermination of sulphur in organic compounds containing other acid-forming elements. The method depends upon reaction of the sulphuric acid, produced from oxygen-flask combustion of organosulphur compounds, with a known and excessive amount of saturated barium bromate solution which on precipitating barium sulphate releases an equivalent amount of bromic acid. On addition of acetone to the solution the excess of barium bromate is then precipitated and, after filtration, is

---

* Present address: Institut für Organische Chemie, Analytische Abteilung, Universität des Saarlandes, 66 Saarbrücken, W. Germany.

redissolved in hot water and determined iodometrically in the presence of acid and an excess of iodide.

EXPERIMENTAL

Reagents

All the reagents were of analytical grade: saturated bromine water, hydrogen peroxide, sodium thiosulphate (0·02–0·04*N*), potassium iodide, starch, acetone and saturated solution of barium bromate monohydrate.

Barium bromate was prepared by adding a hot aqueous solution of potassium bromate slowly and with stirring to a hot aqueous solution containing sufficient barium chloride for stoichiometric reaction. The solution was stirred for 20 min, the precipitate washed by decantation with five or six 500-ml portions of distilled water, filtered off on a Büchner funnel, dried at room temperature and stored.

Apparatus

A 250-ml oxygen combustion flask and ordinary microanalytical equipment.

Procedure

Weigh exactly 3–6 mg of the organosulphur compound and wrap it as usual with the Schöniger technique. Place 10 ml of doubly distilled water in the 250-ml flask, fill the flask with oxygen and quickly add 1 ml of saturated bromine water or 3 or 4 drops of 100-volume hydrogen peroxide. Light the paper fuse, insert the stopper rapidly and invert the flask, holding it and stopper firmly together. When the combustion is complete shake for 5 min, after which the cloud of sulphur trioxide completely disappears. Open the flask and rinse down the stopper and gauze with about 10 ml of doubly distilled water. Place the flask on a hot-plate and boil gently until the volume of the solution has been reduced to 2–4 ml.

While the solution is still hot, add dropwise 2 ml of the saturated barium bromate solution with continuous swirling for 1 min and then cool the flask under running water. Add 50 ml of acetone and filter into a 250-ml conical flask by suction through a sintered glass filter (porosity 4). Wash the precipitate with 10 ml of acetone and remove the filtrate from the conical flask. Redissolve the unreacted excess of barium bromate on the disc, washing it into the conical flask with 50 ml of hot water. To the cold solution add 5 ml of 6*M* hydrochloric acid and an excess of potassium iodide. Titrate the liberated iodine with standardized sodium thiosulphate solution, using starch as indicator. Carry out a blank experiment, using an equal volume of the barium bromate solution.

Since the overall reaction sequence corresponds to

$$SO_4^{2-} \equiv 2BrO_3^- \equiv 12I^- \equiv 12S_2O_3^{2-},$$

the percentage of sulphur in the organic compound is easily calculated from the equation:

$$\%S = \frac{(Y - X).N.32{\cdot}07}{W.12} \times 100$$

where *Y* and *X* are the volumes of thiosulphate (ml) used in the blank and actual determinations respectively, *N* is the normality of the thiosulphate solution, and *W* is the weight (mg) of the organic compound.

RESULTS AND DISCUSSION

The iodometric determination of sulphur in organic compounds is based on complete conversion of the sulphur combustion products into sulphuric acid, which is allowed to undergo a precipitation reaction with a known excess of barium bromate solution. The unreacted barium bromate is precipitated by addition of a water-miscible organic solvent, filtered and redissolved in hot water.

Two possibilities exist for the estimation of sulphuric acid. In one, it can be determined directly with a 12-fold iodometric amplification reaction via estimation of the liberated bromic acid. In the other, the sulphuric acid can be indirectly determined, also with a 12-fold iodometric amplification reaction, but this time *via* estimation of the unreacted excess of barium bromate after its separation and dissolution in hot water.

Barium bromate was selected as the displacement reagent as it is sufficiently soluble in aqueous solutions (7·96 mg/ml at 20° and 56·7 mg/ml at 100°). This appreciable solubility of the salt has a number of advantages

(*i*) It assists the rapid and quantitative reaction with the sulphate ion so that 1 min was found to be quite long enough for completion of the precipitation.

(*ii*) It allows the use of very small volumes of barium bromate solution which helps to minimise the dilution difficulties usually encountered in the quantitative precipitation of the sulphate ion on the micro-scale. As little as 2 ml of the saturated barium bromate solution proved quite satisfactory throughout this work. As expected, this amount was found to greatly exceed that required for the quantitative reaction with the sulphuric acid arising from ignition of micro-amounts of the various organosuphur compounds analysed.

Preliminary experiments revealed that the acidity arising from combustion of organosulphur compounds, whether containing other acid-forming elements or not, was sufficient for quantitative precipitation of the sulphate, and that the addition of more strong acid was unnecessary.

The next step was quantitative precipitation of the remaining excess of unreacted barium bromate (essential before an iodometric finish can be used). One solution is addition of a water-miscible organic solvent which is not oxidized by bromic acid or barium bromate. Several such solvents, *e.g.*, alcohols, dioxan and acetone were tried, and acetone was found to be best, at concentrations above 80%, when the solubility of barium bromate drops to a minimum of 0·0076 mg/ml.

Attempts to estimate the liberated bromic acid directly, after the addition of acetone and without filtering off the precipitates of barium sulphate and bromate, did not succeed, mainly because the reaction with iodide was very slow in the presence of large amounts of acetone. In such media, the reaction goes to completion only after the addition of a few drops of ammonium molybdate catalyst and an excess of acid. The latter unfortunately causes the unreacted barium bromate precipitate to dissolve.

The indirect determination of sulphuric acid *via* iodometric estimation of the excess of unreacted barium bromate, which is easily and quantitatively separated from the aqueous medium by addition of acetone, was then tried. On filtering off the precipitate and redissolving it in hot water, a pure solution of the unreacted barium bromate is obtained. Addition of an excess of iodide and acid to this liberates a 12-fold amount of iodine which may be titrated with thiosulphate as usual. With this indirect method, no correction factor is required to account for the slight solubility of barium bromate because this is almost compensated for in the blank determination.

On applying the procedure for the analysis of compounds containing C, H, and S or C, H, O, and S, accurate results (*cf.* Table I) were obtained. *p*-Toluenesulphonic acid was used as test compound, for which representative figures are given in the Table. Duplicate analyses of dibenzylsulphide and *o*-mercaptobenzoic acid also gave very satisfactory values, indicating the efficiency of the procedure.

INTERFERENCES

Under the prevailing combustion and absorption conditions chlorine, bromine and nitrogen are converted to HCl, $HBr–Br_2$, and HNO_3–nitrogen oxides respectively. Of these, bromine is added in the procedure to oxidize the sulphur combustion products. Further, the excess of bromine, the HBr, CO_2 and oxides of nitrogen, are completely eliminated in the boiling step normally involved in the procedure to concentrate the absorption solution prior to addition of the barium bromate.

TABLE I.—THE IODOMETRIC MICRODETERMINATION OF SULPHUR IN ORGANOSULPHUR COMPOUNDS USING AN AMPLIFICATION REACTION

Compound	Weight, *mg*	Sulphur, % Calc.	Sulphur, % Found
p-Toluenesulphonic acid	2·640	16·86	17·0
	3·775		16·7
	4·065		16·9
	3·235		17·0
	3·865		16·8
o-Mercaptobenzoic acid	2·770	20·80	21·0
	6·785		20·7
Dibenzylsulphide	6·475	14·96	15·1
	4·245		15·2
β,β'-Diaminodiethyldisulphide dihydrochloride	3·425	28·48	28·3
	4·050		28·3
p-Chlorothiophenol	6·020	22·17	22·0
	5·655		22·0
2-Mercaptoimidazole	4·700	32·02	31·9
	5·030		31·9
L-Cysteine	4·120	26·69	26·8
	3·300		26·7
Cysteine hydrochloride	2·755	20·34	20·2
	3·780		20·4

However, a series of determinations was carried out using solutions containing micro-amounts of sulphuric acid alone and in mixture with micro-amounts of hydrochloric, hydrobromic, and/or nitric acids. Running these solutions through the whole procedure showed that the presence of small amounts of these acids did not interfere.

Application of the procedure for the analysis of a variety of organosulphur compounds containing chlorine, nitrogen, or both, gave very satisfactory results (*cf.* Table I). The average absolute error for all the results included in Table I is $\pm 0{\cdot}1_3\%$ and the maximum deviation is $\pm 0{\cdot}2_5\%$.

Organosulphur compounds containing phosphorus or iodine were not available during this study. However, since phosphorus is converted under the present conditions into orthophosphoric acid,[12,13] mixtures containing micro-amounts of sulphuric and orthophosphoric acids were run through the normal procedure. These experiments showed that sulphate could be determined accurately in the presence of phosphate if the precipitation step is conducted within 1 min, followed by rapid addition of the 50 ml acetone to precipitate the excess of barium bromate. In this way, co-precipitation of barium phosphate is minimized.

Similarly, iodine is not expected to interfere in the procedure, mainly because with bromine–water as the absorbent, the iodine combustion products absorbed would be almost expelled from the aqueous sulphuric acid solution in the boiling step.

The procedure described extends the application of the attractive iodometric titration to elemental sulphur microanalysis. The clear advantages of the method are the high sensitivity due to the 12-fold amplification, and the sharp end-point which overcomes the difficulties encountered with the indicator Thorin sometimes used for the direct titration of sulphate with barium ion.[1] In series analysis one determination requires about 30 min.

Zusammenfassung—Eine neue Methode zur jodometrischen Mikrobestimmung von Schwefel in organischen Verbindungen wird beschrieben. Nach der Verbrennung im Sauerstoffkolben wird eine zwölffache Verstärkungsreaktion verwendet. Sie beruht auf der Reaktion der entstandenen Schwefelsäure mit einem Überschuß an gesättigter Bariumbromatlösung. Das nicht verbrauchte Bariumbromat wird durch Zugabe von Aceton ausgefällt, abfiltriert und in heißem Wasser wieder gelöst; nach Zugabe von überschüssigem Jodid und Säure wird das freigesetzte Jod mit Thiosulfat titriert. Die Methode ist einfach, schnell, sehr genau und hat umfangreiche Anwendungsmöglichkeiten bei der Mikroanalyse von schwefelhaltigen organischen Verbindungen, die andere säurebildende Elemente enthalten.

Résumé—On décrit une nouvelle méthode pour la microdétermination iodométrique du soufre dans les composés organiques, utilisant une réaction d'amplification de facteur 12 après combustion en fiole d'oxygène. La méthode est basée sur la réaction de l'acide sulfurique résultant avec un excès de solution saturée de bromate de baryum. Le bromate de baryum qui n'a pas réagi est précipité par addition d'acétone, filtré, redissous dans l'eau chaude et, après addition d'un excès d'iodure et d'acide, on titre l'iode libéré par le thiosulfate. La méthode est simple, rapide, hautement précise et d'une large application dans la microanalyse de composés organosulfurés contenant d'autres éléments communs formant des acides.

REFERENCES

1. H. Wagner, *Mikrochim. Acta*, 1957, 19.
2. I. Lysyj and J. E. Zarembo, *Anal. Chem.*, 1958, **30**, 428.
3. R. Ottosson and O. Snellman, *Acta Chem. Scand.*, 1957, **11**, 185.
4. L. Gildenberg, *Microchem. J.*, 1959, **3**, 167.
5. R. N. Boos, *Analyst*, 1959, **84**, 633.
6. L. W. Andrews, *Am. Chem. J.*, 1890, **11**, 567.
7. B. I. Sojbelman, *Zh. Analit. Khim.*, 1948, **3**, 258.
8. L. Erdey and E. Banyai, *Z. Anal. Chem.*, 1958, **161**, 16.
9. B. Jaselskis and S. F. Vas, *Anal. Chem.*, 1964, **36**, 1965.
10. T. S. Prokopov, *Mikrochim. Acta*, 1968, 675.
11. Y. A. Gawargious and A. B. Farag, Unpublished work.
12. *Idem*, *Microchem. J.*, 1971, **16**, 333.
13. *Idem*, *ibid.*, 1971, **16**, 342.

Talanta, 1972, Vol. 19, pp. 641 to 645. Pergamon Press. Printed in Northern Ireland

IODOMETRIC MICRODETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS BY AN AMPLIFICATION REACTION

Y. A. GAWARGIOUS* and A. B. FARAG
Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, U.A.R.

(*Received* 31 *March* 1971. *Accepted* 8 *July* 1971)

Summary—A new method is described for the iodometric microdetermination of sulphur in organic compounds, using a 12-fold amplification reaction after oxygen-flask combustion. The method is based on reaction of the resulting sulphuric acid with an excess of saturated barium bromate solution. The unreacted barium bromate is precipitated by addition of acetone, filtered off, redissolved in hot water and after addition of an excess of iodide and acid, the iodine liberated is titrated with thiosulphate. The method is simple, rapid, highly accurate, and of wide application in the microanalysis of organosulphur compounds containing other common acid-forming elements.

SEVERAL methods are available in the literature for the determination of sulphur in organic compounds *via* sulphate estimation.[1–5] Redox titration methods after precipitation as barium sulphate, with slightly soluble salts such as barium iodate or chromate, were suggested by Andrews[6] and Sojbelman[7] and described in greater detail by Erdey and Banyai.[8] In a recent publication, Jaselskis and Vas[9] revived the barium iodate method for the semimicro determination of the sulphate ion in synthetic inorganic mixtures. They determined sulphate iodometrically, using a 3-hr equilibration of the sulphate solution with solid barium iodate in 40% acetone–0·1*M* aqueous acetic acid mixture. The liberated iodate was determined iodometrically after separation of the mixed precipitates of barium sulphate and barium iodate. Although an amplified iodometric reaction is involved, the procedure is time-consuming, and is not suitable for the microdetermination of sulphur in organic compounds.

Recently, Prokopov[10] published a method for the iodometric microdetermination of sulphur in organic compounds containing C, H, O, and S. The method is based upon combustion in the oxygen flask, with use of aqueous hydrogen peroxide as absorbant to convert sulphur combustion products into sulphuric acid. Addition of an excess of potassium iodide and iodate to the solution liberates iodine which is then titrated with thiosulphate. Unfortunately, this method cannot be used when other acid-forming elements are present in the organic compound. Various attempts[11] have been made to eliminate such interferences but the procedures tend to be rather lengthy and complicated and were thus ignored.

In the present investigation a new amplification method is described for the iodometric microdetermination of sulphur in organic compounds containing other acid-forming elements. The method depends upon reaction of the sulphuric acid, produced from oxygen-flask combustion of organosulphur compounds, with a known and excessive amount of saturated barium bromate solution which on precipitating barium sulphate releases an equivalent amount of bromic acid. On addition of acetone to the solution the excess of barium bromate is then precipitated and, after filtration, is

---

* Present address: Institut für Organische Chemie, Analytische Abteilung, Universität des Saarlandes, 66 Saarbrücken, W. Germany.

redissolved in hot water and determined iodometrically in the presence of acid and an excess of iodide.

EXPERIMENTAL

Reagents

All the reagents were of analytical grade: saturated bromine water, hydrogen peroxide, sodium thiosulphate (0·02–0·04*N*), potassium iodide, starch, acetone and saturated solution of barium bromate monohydrate.

Barium bromate was prepared by adding a hot aqueous solution of potassium bromate slowly and with stirring to a hot aqueous solution containing sufficient barium chloride for stoichiometric reaction. The solution was stirred for 20 min, the precipitate washed by decantation with five or six 500-ml portions of distilled water, filtered off on a Büchner funnel, dried at room temperature and stored.

Apparatus

A 250-ml oxygen combustion flask and ordinary microanalytical equipment.

Procedure

Weigh exactly 3–6 mg of the organosulphur compound and wrap it as usual with the Schöniger technique. Place 10 ml of doubly distilled water in the 250-ml flask, fill the flask with oxygen and quickly add 1 ml of saturated bromine water or 3 or 4 drops of 100-volume hydrogen peroxide. Light the paper fuse, insert the stopper rapidly and invert the flask, holding it and stopper firmly together. When the combustion is complete shake for 5 min, after which the cloud of sulphur trioxide completely disappears. Open the flask and rinse down the stopper and gauze with about 10 ml of doubly distilled water. Place the flask on a hot-plate and boil gently until the volume of the solution has been reduced to 2–4 ml.

While the solution is still hot, add dropwise 2 ml of the saturated barium bromate solution with continuous swirling for 1 min and then cool the flask under running water. Add 50 ml of acetone and filter into a 250-ml conical flask by suction through a sintered glass filter (porosity 4). Wash the precipitate with 10 ml of acetone and remove the filtrate from the conical flask. Redissolve the unreacted excess of barium bromate on the disc, washing it into the conical flask with 50 ml of hot water. To the cold solution add 5 ml of 6*M* hydrochloric acid and an excess of potassium iodide. Titrate the liberated iodine with standardized sodium thiosulphate solution, using starch as indicator. Carry out a blank experiment, using an equal volume of the barium bromate solution.

Since the overall reaction sequence corresponds to

$$SO_4^{2-} \equiv 2BrO_3^- \equiv 12I^- \equiv 12S_2O_3^{2-},$$

the percentage of sulphur in the organic compound is easily calculated from the equation:

$$\%S = \frac{(Y - X) . N . 32{\cdot}07}{W . 12} \times 100$$

where Y and X are the volumes of thiosulphate (ml) used in the blank and actual determinations respectively, N is the normality of the thiosulphate solution, and W is the weight (mg) of the organic compound.

RESULTS AND DISCUSSION

The iodometric determination of sulphur in organic compounds is based on complete conversion of the sulphur combustion products into sulphuric acid, which is allowed to undergo a precipitation reaction with a known excess of barium bromate solution. The unreacted barium bromate is precipitated by addition of a water-miscible organic solvent, filtered and redissolved in hot water.

Two possibilities exist for the estimation of sulphuric acid. In one, it can be determined directly with a 12-fold iodometric amplification reaction via estimation of the liberated bromic acid. In the other, the sulphuric acid can be indirectly determined, also with a 12-fold iodometric amplification reaction, but this time *via* estimation of the unreacted excess of barium bromate after its separation and dissolution in hot water.

Barium bromate was selected as the displacement reagent as it is sufficiently soluble in aqueous solutions (7·96 mg/ml at 20° and 56·7 mg/ml at 100°). This appreciable solubility of the salt has a number of advantages

(*i*) It assists the rapid and quantitative reaction with the sulphate ion so that 1 min was found to be quite long enough for completion of the precipitation.

(*ii*) It allows the use of very small volumes of barium bromate solution which helps to minimise the dilution difficulties usually encountered in the quantitative precipitation of the sulphate ion on the micro-scale. As little as 2 ml of the saturated barium bromate solution proved quite satisfactory throughout this work. As expected, this amount was found to greatly exceed that required for the quantitative reaction with the sulphuric acid arising from ignition of micro-amounts of the various organosuphur compounds analysed.

Preliminary experiments revealed that the acidity arising from combustion of organosulphur compounds, whether containing other acid-forming elements or not, was sufficient for quantitative precipitation of the sulphate, and that the addition of more strong acid was unnecessary.

The next step was quantitative precipitation of the remaining excess of unreacted barium bromate (essential before an iodometric finish can be used). One solution is addition of a water-miscible organic solvent which is not oxidized by bromic acid or barium bromate. Several such solvents, *e.g.*, alcohols, dioxan and acetone were tried, and acetone was found to be best, at concentrations above 80%, when the solubility of barium bromate drops to a minimum of 0·0076 mg/ml.

Attempts to estimate the liberated bromic acid directly, after the addition of acetone and without filtering off the precipitates of barium sulphate and bromate, did not succeed, mainly because the reaction with iodide was very slow in the presence of large amounts of acetone. In such media, the reaction goes to completion only after the addition of a few drops of ammonium molybdate catalyst and an excess of acid. The latter unfortunately causes the unreacted barium bromate precipitate to dissolve.

The indirect determination of sulphuric acid *via* iodometric estimation of the excess of unreacted barium bromate, which is easily and quantitatively separated from the aqueous medium by addition of acetone, was then tried. On filtering off the precipitate and redissolving it in hot water, a pure solution of the unreacted barium bromate is obtained. Addition of an excess of iodide and acid to this liberates a 12-fold amount of iodine which may be titrated with thiosulphate as usual. With this indirect method, no correction factor is required to account for the slight solubility of barium bromate because this is almost compensated for in the blank determination.

On applying the procedure for the analysis of compounds containing C, H, and S or C, H, O, and S, accurate results (*cf.* Table I) were obtained. *p*-Toluenesulphonic acid was used as test compound, for which representative figures are given in the Table. Duplicate analyses of dibenzylsulphide and *o*-mercaptobenzoic acid also gave very satisfactory values, indicating the efficiency of the procedure.

INTERFERENCES

Under the prevailing combustion and absorption conditions chlorine, bromine and nitrogen are converted to HCl, $HBr-Br_2$, and HNO_3–nitrogen oxides respectively. Of these, bromine is added in the procedure to oxidize the sulphur combustion products. Further, the excess of bromine, the HBr, CO_2 and oxides of nitrogen, are completely eliminated in the boiling step normally involved in the procedure to concentrate the absorption solution prior to addition of the barium bromate.

TABLE I.—THE IODOMETRIC MICRODETERMINATION OF SULPHUR IN ORGANOSULPHUR COMPOUNDS USING AN AMPLIFICATION REACTION

Compound	Weight, *mg*	Sulphur, % Calc.	Sulphur, % Found
p-Toluenesulphonic acid	2·640	16·86	17·0
	3·775		16·7
	4·065		16·9
	3·235		17·0
	3·865		16·8
o-Mercaptobenzoic acid	2·770	20·80	21·0
	6·785		20·7
Dibenzylsulphide	6·475	14·96	15·1
	4·245		15·2
β,β'-Diaminodiethyldisulphide dihydrochloride	3·425	28·48	28·3
	4·050		28·3
p-Chlorothiophenol	6·020	22·17	22·0
	5·655		22·0
2-Mercaptoimidazole	4·700	32·02	31·9
	5·030		31·9
L-Cysteine	4·120	26·69	26·8
	3·300		26·7
Cysteine hydrochloride	2·755	20·34	20·2
	3·780		20·4

However, a series of determinations was carried out using solutions containing micro-amounts of sulphuric acid alone and in mixture with micro-amounts of hydrochloric, hydrobromic, and/or nitric acids. Running these solutions through the whole procedure showed that the presence of small amounts of these acids did not interfere.

Application of the procedure for the analysis of a variety of organosulphur compounds containing chlorine, nitrogen, or both, gave very satisfactory results (*cf.* Table I). The average absolute error for all the results included in Table I is $\pm 0{\cdot}1_3\%$ and the maximum deviation is $\pm 0{\cdot}2_5\%$.

Organosulphur compounds containing phosphorus or iodine were not available during this study. However, since phosphorus is converted under the present conditions into orthophosphoric acid,[12,13] mixtures containing micro-amounts of sulphuric and orthophosphoric acids were run through the normal procedure. These experiments showed that sulphate could be determined accurately in the presence of phosphate if the precipitation step is conducted within 1 min, followed by rapid addition of the 50 ml acetone to precipitate the excess of barium bromate. In this way, co-precipitation of barium phosphate is minimized.

Similarly, iodine is not expected to interfere in the procedure, mainly because with bromine–water as the absorbent, the iodine combustion products absorbed would be almost expelled from the aqueous sulphuric acid solution in the boiling step.

The procedure described extends the application of the attractive iodometric titration to elemental sulphur microanalysis. The clear advantages of the method are the high sensitivity due to the 12-fold amplification, and the sharp end-point which overcomes the difficulties encountered with the indicator Thorin sometimes used for the direct titration of sulphate with barium ion.[1] In series analysis one determination requires about 30 min.

Zusammenfassung—Eine neue Methode zur jodometrischen Mikrobestimmung von Schwefel in organischen Verbindungen wird beschrieben. Nach der Verbrennung im Sauerstoffkolben wird eine zwölffache Verstärkungsreaktion verwendet. Sie beruht auf der Reaktion der entstandenen Schwefelsäure mit einem Überschuß an gesättigter Bariumbromatlösung. Das nicht verbrauchte Bariumbromat wird durch Zugabe von Aceton ausgefällt, abfiltriert und in heißem Wasser wieder gelöst; nach Zugabe von überschüssigem Jodid und Säure wird das freigesetzte Jod mit Thiosulfat titriert. Die Methode ist einfach, schnell, sehr genau und hat umfangreiche Anwendungsmöglichkeiten bei der Mikroanalyse von schwefelhaltigen organischen Verbindungen, die andere säurebildende Elemente enthalten.

Résumé—On décrit une nouvelle méthode pour la microdétermination iodométrique du soufre dans les composés organiques, utilisant une réaction d'amplification de facteur 12 après combustion en fiole d'oxygène. La méthode est basée sur la réaction de l'acide sulfurique résultant avec un excès de solution saturée de bromate de baryum. Le bromate de baryum qui n'a pas réagi est précipité par addition d'acétone, filtré, redissous dans l'eau chaude et, après addition d'un excès d'iodure et d'acide, on titre l'iode libéré par le thiosulfate. La méthode est simple, rapide, hautement précise et d'une large application dans la microanalyse de composés organosulfurés contenant d'autres éléments communs formant des acides.

REFERENCES

1. H. Wagner, *Mikrochim. Acta*, 1957, 19.
2. I. Lysyj and J. E. Zarembo, *Anal. Chem.*, 1958, **30**, 428.
3. R. Ottosson and O. Snellman, *Acta Chem. Scand.*, 1957, **11**, 185.
4. L. Gildenberg, *Microchem. J.*, 1959, **3**, 167.
5. R. N. Boos, *Analyst*, 1959, **84**, 633.
6. L. W. Andrews, *Am. Chem. J.*, 1890, **11**, 567.
7. B. I. Sojbelman, *Zh. Analit. Khim.*, 1948, **3**, 258.
8. L. Erdey and E. Banyai, *Z. Anal. Chem.*, 1958, **161**, 16.
9. B. Jaselskis and S. F. Vas, *Anal. Chem.*, 1964, **36**, 1965.
10. T. S. Prokopov, *Mikrochim. Acta*, 1968, 675.
11. Y. A. Gawargious and A. B. Farag, Unpublished work.
12. *Idem*, *Microchem. J.*, 1971, **16**, 333.
13. *Idem*, *ibid.*, 1971, **16**, 342.

Talanta, 1972, Vol. 19, pp. 647 to 655. Pergamon Press. Printed in Northern Ireland

IMPROVED SYNTHESIS AND STABILITY OF 8-SELENOQUINOLINE AND ITS SODIUM SALT AS ORGANIC REAGENTS

EIICHI SEKIDO and ISAMU FUJIWARA
Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan

(*Received* 18 *June* 1971. *Accepted* 14 *July* 1971)

Summary—The synthesis of 8-selenoquinoline and its sodium salt has been improved by optimization of each process. The stability of the reagents in air and nitrogen has been examined and correlated with the drying method. Both 8-selenoquinoline and its sodium salt can exist as the monohydrate. It was found that the sodium salt of 8-selenoquinoline monohydrate is best as the weighing form of the reagent and that it can be kept stable under nitrogen in a vessel containing silica gel.

8-SELENOQUINOLINE (8-quinolineselenol), so-called selenoxine, was synthesized by Sekido, Fernando and Freiser,[1] and the properties of this reagent and some of its metal chelates were studied.[2–4] Because of the poor yield and its instability in air, however, further studies appeared necessary.

Hitherto, 8-selenoquinoline has been synthesized according to scheme I. The diazotization of 8-aminoquinoline proceeds successfully in mineral acid but the resulting diazonium salt solution does not necessarily react smoothly with potassium selenocyanate; consequently the yield of 8-selenoquinoline or 8,8′-diquinolyldiselenide is usually poor. 8-Selenoquinoline is so unstable in air that it is necessary to take care in storing it, and on the other hand 8,8′-diquinolyldiselenide must be reduced just before use.

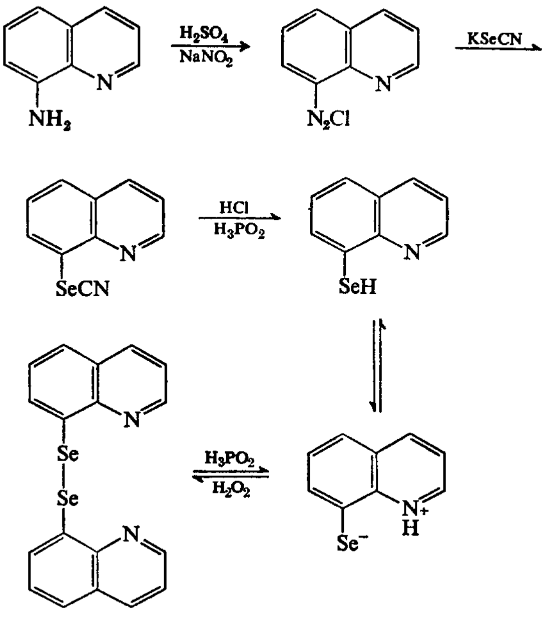
This paper deals with the improved synthesis of 8-selenoquinoline and the stability of 8-selenoquinoline and its sodium salt as a function of the drying method used.

EXPERIMENTAL

Synthesis of 8-selenoquinoline and its sodium salt

8-Selenocyanatoquinoline. Pure 8-aminoquinoline (15 g, 0·105 mole) prepared from 8-hydroxyquinoline,[3] is dissolved in 48% hydrobromic acid (78 ml, 0·50 mole) and water (200 ml). Into the solution cooled to 0°, 10% sodium nitrite solution is dropped with stirring. A colour change from red to yellow-green indicates the end of the diazotization. The excess of nitrite is destroyed by addition of 2*M* sulphamic acid until evolution of nitrogen ceases. The diazonium solution is neutralized with solid sodium acetate to pH 1·5–2·0, in an ice-bath. Then 15% potassium selenocyanate solution (100 ml, 0·104 mole) is added slowly during one hour, at below 5°. The bulky yellow-brown product is formed as a suspension and nitrogen is evolved. To complete the reaction, the solution is stirred for 30 min at below 5° and then for several hours at room temperature (in a fume-cupboard). The solution is adjusted to pH 8·0 with 12*M* sodium hydroxide and the precipitate filtered off. If 1% hydrogen peroxide solution is added to the filtrate, a little yellow-brown precipitate may be formed. This precipitate, probably impure 8,8′-diquinolyldiselenide, is added to the 8-selenocyanatoquinoline in the following procedure. 8-Selenocyanatoquinoline can be recrystallized from 50% v/v aqueous methanol (to give yellow-brown needles, m.p. 74–75°), but as it is an evil-smelling compound and the recrystallization is difficult, the crude compound is used in the following procedure.

8,8′-Diquinolyldiselenide. The crude 8-selenocyanatoquinoline (10 g, 0·043 mole) is dissolved in 6*M* hydrochloric acid (50 ml) and 50% hypophosphorous acid (10 ml) and the resulting solution is warmed for about 15 min on a water-bath. The colour changes gradually from yellow to red, which indicates the formation of 8-selenoquinoline by hydrolysis of 8-selenocyanatoquinoline. After cooling in an ice-bath, the impurity is filtered off (in a fume-cupboard, because hydrogen cyanide gas may



Scheme I

be produced). The 8-selenoquinoline in acid solution is neutralized with 5*M* sodium hydroxide in an ice-bath while nitrogen is bubbled through the solution. The colour changes to red-violet in weakly acidic or neutral solution and then to yellow in alkaline solution. The alkaline solution of 8-selenoquinoline is rapidly filtered under nitrogen to remove the impurities. When 1% hydrogen peroxide solution is added to the filtrate, a white precipitate of 8,8′-diquinolyldiselenide forms rapidly. The precipitate is filtered off, washed with water and dried *in vacuo* at room temperature. It is purified by dissolving it in hydrochloric and hypophosphorous acids and repeating the above-mentioned procedure. Yield, 40% (from 8-aminoquinoline); fine white crystals, m.p. 205° (lit.,[1] 205–206°). Calculated for $C_{18}H_{12}N_2Se_2$: C, 52·19%; H, 2·92%; N, 6·76%. Found: C, 52·6%; H, 3·0%; N, 7·3%.

8-Selenoquinoline. Purified 8,8′-diquinolyldiselenide (15 g) is dissolved in as little 6*M* hydrochloric acid as possible and 50% hypophosphorous acid (5 ml). The colour changes from yellow to red, which indicates the formation of 8-selenoquinoline. To complete the reduction the solution is warmed on a water-bath for about 10 min. It is not favourable to heat at high temperature and for a long time. After cooling, the solution is filtered if necessary, put in an ice-bath, and kept under nitrogen while 12*M* sodium hydroxide is added dropwise. The red solution becomes deep violet-red and then a precipitate forms, which redissolves on further addition of sodium hydroxide, to give a yellow solution, which is rapidly filtered if necessary. Then 2*M* hydrochloric acid is carefully added until the pH reaches 4, and dark red-brown needles precipitate. The precipitate is rapidly filtered off under nitrogen and washed with oxygen-free cold water. The 8-selenoquinoline is dried and kept in a desiccator containing silica gel and filled with nitrogen. More product can be obtained by repeating the procedure with the filtrate and washings. Yield, 52%; red-brown needles, m.p. not measurable (oxidation to 8,8′-diquinolyldiselenide). Calculated for C_9H_7NSe: C, 51·94%; H, 3·39%. Found: C, 51·7%; H, 3·6%.

Sodium salt of 8-selenoquinoline. When 12*M* sodium hydroxide is added to an acidic solution of 8-selenoquinoline, in an ice-bath under nitrogen, the yellow sodium salt of 8-selenoquinoline is precipitated. After filtration, the sodium salt is dried and recrystallized from 95% ethanol at least thrice. The amount of water of crystallization depends on the method of drying. Drying and storage in a desiccator containing silica gel and filled with nitrogen yields the monohydrate. Yield, 21·0% (from 8,8′-diquinolyldiselenide); yellow crystals, Calculated for $C_9H_8NOSeNa$: C, 43·57%; H, 3·25%. Found: C, 43·3%; H, 3·6%.

When the salt is dried *in vacuo* at 120°, the anhydride is obtained. Yellow crystals; Calculated for C_9H_6NSeNa: C, 46·98%; H, 2·63%; N, 6·09%. Found: C, 46·7%; H, 2·9%; N, 5·9%.

Other reagents

8-Mercaptoquinoline was prepared by the method of Kealey and Freiser[5] and its sodium salt by the method of Nakamura and Sekido.[4]

Apparatus

Drying. Vacuum desiccators containing silica gel or calcium chloride as desiccant were used for drying at room temperature and an electric oven under reduced pressure for drying by heating.

RESULTS AND DISCUSSION

Synthesis of 8-selenoquinoline

The improvements in the synthesis of 8-selenoquinoline are summarized in Table I.

TABLE I.—IMPROVEMENTS OF THE SYNTHESIS OF 8-SELENOQUINOLINE COMPARED WITH THE CONVENTIONAL METHOD

Reaction parameter	This method	Conventional method[1]
Acidity of diazotization	Mineral acids (HCl, HBr or H_2SO_4) 0·25*M*	H_2SO_4, 0·1*M*
Neutralization of diazonium salt solution	Addition of solid sodium acetate	Addition of 5*M* sodium hydroxide
Acidity of diazonium salt solution and KSeCN solution	pH 1·5–2·5	pH 7·0
Order of addition	Addition of KSeCN to diazonium salt solution	Addition of diazonium salt solution to KSeCN solution
Temperature and time of the reaction	30 min in an ice-bath and then 60 min at room temperature	30 min in an ice-bath
Yield of 8,8′-diquinolyldiselenide from 8-aminoquinoline	40%	12% (Maximum)

Effect of acidity on the diazotization of 8-aminoquinoline. It was found that the diazotization proceeds in hydrochloric or hydrobromic acid as well as in sulphuric acid and that at least 5 equivalents of acid per equivalent of 8-aminoquinoline are needed for smooth diazotization.

Neutralization of diazonium salt of 8-aminoquinoline. When 5*M* sodium hydroxide is used for neutralization to pH 1·5–2·5, higher pH values may be attained locally. In addition, heating by the exothermic reaction might accelerate decomposition of the diazonium salt. Use of more dilute sodium hydroxide solution makes the volume too large, and causes difficulty later. Addition of solid sodium acetate eliminates these disadvantages.

Acidity of the diazonium salt solution and the potassium selenocyanate solution. Potassium selenocyanate decomposes in acid solution to yield colloidal red selenium.

The rate of decomposition as a function of pH is as follows:

pH	below 1	1·0	2·0	4·0	5·0	7·0
Decomposition time, *min*	instantly	2	5–6	5–6	10	no change

The decomposition is accelerated by increase in temperature.

Although the diazonium salt of 8-aminoquinoline is stable in strongly acidic solution, it decomposes at higher pH. The yield of 8,8′-diquinolyldisulphide by reaction of the diazonium salt with thiourea was used to monitor the effect of pH on decomposition of the diazonium salt (the rate of reaction of the urea increases with pH, so an inverse relationship of yield to pH indicates faster decomposition as the pH is increased):

pH	−0·4	1·0	2·0	4·0	5·0	7·0
Yield, %	50	40	32	19	7	9

The best compromise between decomposition of the diazonium salt and of potassium selenocyanate was to use a pH of 1·5–2·5.

Order of addition of the diazonium salt and selenocyanate. If the neutralized diazonium salt solution is added to the selenocyanate solution,[1] the product becomes very tarry and difficult to remove. The reverse order of addition was found to give a readily filterable yellow-brown precipitate.

Drying conditions. The effect of varying the drying conditions is shown in Table II.

TABLE II.—WATER CONTENT AND COLOUR OF 8-SELENOQUINOLINE AND ITS SODIUM SALT WHEN THESE ARE DRIED UNDER VARIOUS CONDITIONS

		Drying condition					
No.	Substance	Desiccant	Atmosphere	Temp., *°C*	Time, *hr*	Water content,* %	Colour
1	8-SQ†	silica gel	nitrogen	20–25	24	8·2	red
2	8-SQ†	silica gel	nitrogen	20–25	48	0	red-brown
3	8-SQ†	silica gel	vacuum (0·1 μbar)	20–25	24	0	red-brown
4	8-SQ†	$CaCl_2$	nitrogen	20–25	48	0	red-brown
5	8-SQ-Na‡	silica gel	vacuum (0·1 μbar)	20–25	24	6·7	yellow
6	8-SQ-Na‡	silica gel	(0·1 μbar)	20–25	48	7·6	yellow
7	8-SQ-Na‡	silica gel	(0·1 μbar)	20–25	7 days	7·2	yellow
8	8-SQ-Na‡	silica gel	25–40 mbar	20–25	48	7·8	yellow
9	8-SQ-Na‡	no	vacuum (0·1 μbar)	120	1–6	0	orange

* Average value of at least 5 results. Range ±0·5%. One molecule of water of crystallization corresponds to 8·0% H_2O for 8-SQ and 7·3% for 8-SQ-Na.

† 8-SQ: 8-selenoquinoline.

‡ 8-SQ-Na: sodium salt of 8-selenoquinoline.

Experiments 1–4 show that 8-selenoquinoline easily loses its water of crystallization. In contrast, the sodium salt exists as the monohydrate over a fairly wide range of drying conditions. The anhydrous salt is so hygroscopic that it must be kept in a desiccator containing phosphorus pentoxide.

Thermal stability of 8-selenoquinoline and its sodium salt

8-Selenoquinoline, especially its monohydrate, is easily oxidized in air to 8,8′-diquinolyldiselenide. Therefore, its thermal stability was examined in nitrogen as well as in air. Thermogravimetry of 8-selenoquinoline monohydrate in air (curve *A* in Fig. 1) shows loss of the water at a temperature of 51° or lower, accompanied by a colour change to red-brown at 50–51°. These facts may support the hypothesis that the water is not adsorbed by 8-selenoquinoline but weakly bound to it as shown in structure **I**. Bankovskii, Chera and Ievin'sh[6] proposed structure **II** for 8-mercaptoquinoline dihydrate. Considering the difference in the acid dissociation constants[1] of —SH in 8-mercaptoquinoline and —SeH for 8-selenoquinoline (in other words, the difference of electronegativities for sulphur and selenium) the S· · ·H bond in **II** may be stronger than the Se· · ·H bond in **I**.

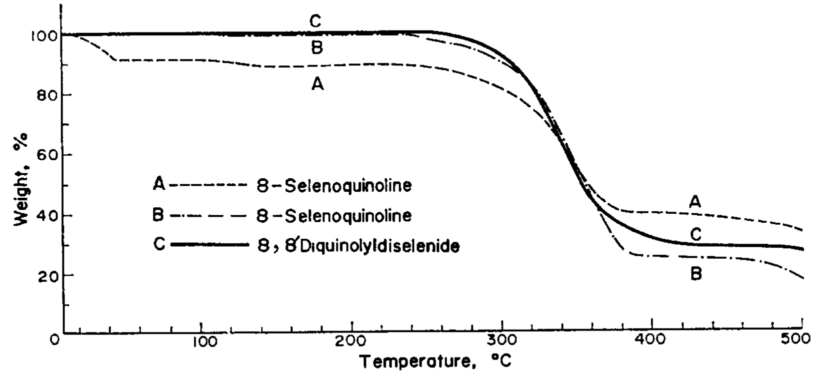
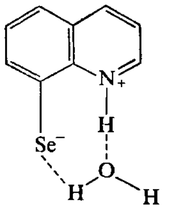
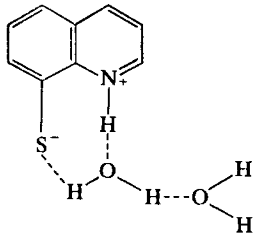


FIG. 1.—Thermogravimetric curves of 8-selenoquinoline and 8,8′-diquinolyldiselenide in air.



I



II

Therefore, the temperature of dehydration for 8-mercaptoquinoline (58–59°) should be higher than that for 8-selenoquinoline (51°). In the case of 8-mercaptoquinoline, the second water molecule may be weakly connected *via* a hydrogen bond to the cyclically bound water molecule.

The anhydride (curve *A* above 50° and curve *B* in Fig. 1) changes to 8,8′-diquinolyldiselenide by 140° (*cf.* curve *C* in Fig. 1). The oxidation of 8-selenoquinoline is also confirmed by the identity or the infrared spectra of the product from 8-selenoquinoline heated to 180–190° and of 8,8′-diquinolyldiselenide. The differential thermal analysis (DTA) and thermogravimetric curves of 8-selenoquinoline under nitrogen (curves *A* and A' in Fig. 2) are different from those of 8,8′-diquinolyldiselenide (curves C and C'). The peak at 204° on curve C corresponds to melting of 8,8′-diquinolyldiselenide and that at 360° to decomposition of the quinoline nucleus.

8-Selenoquinoline is completely oxidized to 8,8′-diquinolyldiselenide after 3 hr in air. This oxidation is confirmed by the disappearance of the infrared absorption band at 2925 cm^{-1} (N–H stretching vibration) and by the agreement with the infrared spectrum of 8,8′-diquinolyldiselenide. Anhydrous 8-selenoquinoline is stable for at least three weeks when stored under nitrogen in a vessel containing silica gel.

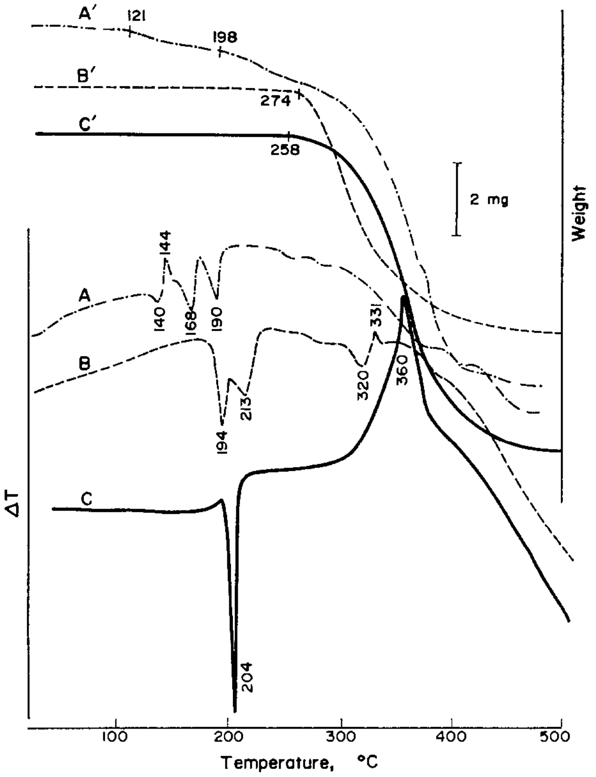
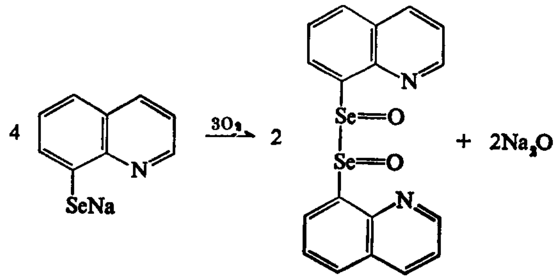


FIG. 2.—Differential thermal curves (A, B and C) and thermogravimetric curves (A′, B′ and C′) of the reagents in nitrogen gas. A and A′: 8-selenoquinoline; B and B′: 8,8′-diquinolyldisulphide; C and C′: 8,8′-diquinolyldiselenide.

Thermogravimetric curves for the sodium salt of 8-selenoquinoline in nitrogen and in air are shown in Fig. 3. The water is all lost between 78 and 106° (curve A). The anhydride increases in weight by 10% over the temperature range 160–190° if heated in air (curves A and B) but not if heated in nitrogen or carbon dioxide (curve C). A similar phenomenon occurs with the sodium salt of 8-mercaptoquinoline,[7] and not for 8-selenoquinoline or 8,8′-diquinolyldiselenide. It is assumed that the sodium salt of 8-selenoquinoline is oxidized by air. Oxidation according to the reaction below gives a theoretical weight increase of 10·4% (experimental value, 10·0%).



The DTA curves for the sodium salts of 8-selenoquinoline monohydrate and 8-mercaptoquinoline dihydrate are shown in Fig. 4; for both there is a large endothermic peak at about 120°, which corresponds to loss of the water. The rest of the decomposition is rather complex. The bond strength between the water and the organic molecule is presumably almost the same for both compounds. The O–H stretching vibration in the infrared spectra for both compounds exists at almost the same position, 3277 cm^{-1} for the 8-selenoquinoline salt and 3200–3300 cm^{-1} for that of 8-mercaptoquinoline, the first being relatively sharp and the other broad (Fig. 5). These facts suggest that the structures may be III and IV respectively.

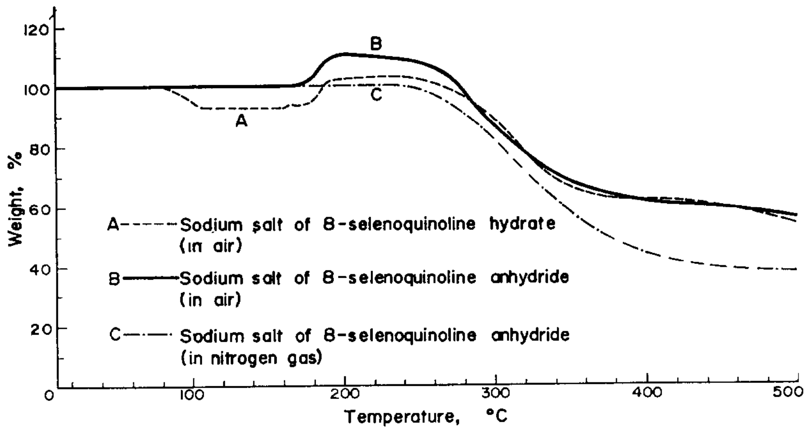
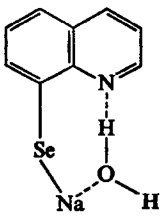
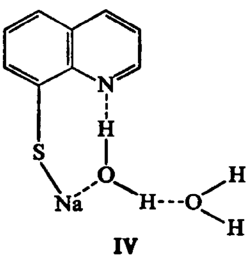


FIG. 3.—Thermogravimetric curves of the sodium salt of 8-selenoquinoline in air and nitrogen.



III



IV

That the dehydration temperature of the sodium salts is higher than that of the 8-seleno- or 8-mercaptoquinoline may be attributed to the bond between the sodium

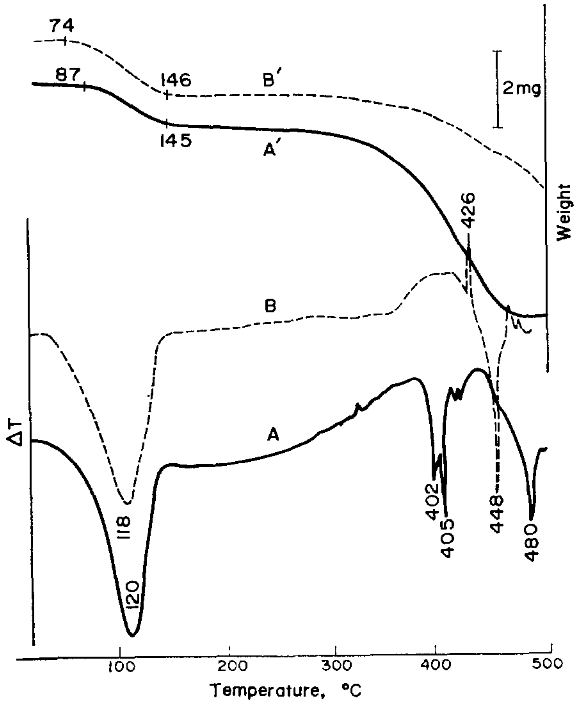


FIG. 4.—Differential thermal curves (A and B) and thermogravimetric curves (A′ and B′) of the reagents in nitrogen gas. A and A′: sodium salt of 8-selenoquinoline; B and B′: sodium salt of 8-mercaptoquinoline.

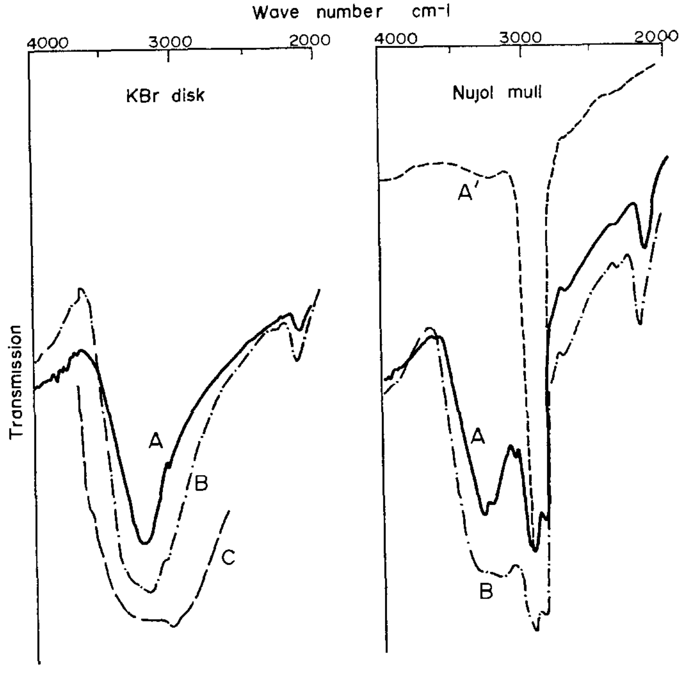


FIG. 5.—Infrared spectra of sodium salt of the reagents in the region of 4000–2000 cm^{-1}. A: 8-selenoquinoline monohydrate; *A′*: its anhydride; B: 8-mercaptoquinoline dihydrate; C: 8-hydroxyquinoline hydrate.

atom and the oxygen atom of water being stronger than that between the oxygen atom and the selenium or the sulphur atom. Furthermore, the similar dehydration temperatures for the sodium salts suggest that one water molecule exists between the sodium atom and the nitrogen atom of the quinoline nucleus in both. The second water molecule of the dihydrate, being bound to the cyclically bound water molecule by a hydrogen bond, will broaden the O—H stretching vibration band.

The temperature of incipient decomposition of the sodium salt of 8-selenoquinoline is lower than that for 8-mercaptoquinoline salt; the S—Na bond may be stronger than the Se—Na bond.

The anhydrous sodium salt of 8-selenoquinoline is so hygroscopic that it abstracts water from silica gel in a desiccator. It is stable if kept in a nitrogen atmosphere over phosphorus pentoxide in a desiccator, but over P_2O_5 in a vacuum it changes gradually into a red-brown compound. The sodium salt monohydrate is the best storage form, being stable for at least 2½ months in a nitrogen atmosphere in a desiccator containing silica gel.

Zusammenfassung—Die Synthese von 8-Selenochinolin und seines Natriumsalzes wurde durch Optimierung jeder Stufe verbessert. Die Stabilität der Reagentien an Luft und Stickstoff wurde geprüft und mit der Trocknungsmethode in Zusammenhand gebracht. Sowohl 8-Selenochinolin als auch sein Natriumsalz können als Monohydrat existieren. Es wurde gefunden, daß das Natriumsalz von 8-Selenochinolin-Monohydrat die beste Wägeform des Reagens darstellt und daß es unter Stickstoff in einem Silicagel enthaltenden Gefäß stabilisiert werden kann.

Résumé—On a amélioré la synthèse de la 8-sélénoquinoléine et de son sel de sodium en optimalisant chaque opération. On a examiné la stabilité des réactifs à l'air et sous azote et on l'a rattachée à la méthode de séchage. La 8-sélénoquinoléine et son sel de sodium peuvent exister à l'état de monohydrate. On a trouvé que le monohydrate du sel de sodium de la 8-sélénoquinoléine est la meilleure forme du réactif pour la pesée et qu'il peut être conservé de manière stable sous azote dans un récipient contenant du gel de silice.

REFERENCES

1. E. Sekido, Q. Fernando and H. Freiser, *Anal. Chem.*, 1964, **36**, 1768.
2. *Idem, ibid.*, 1963, **35**, 1550.
3. *Idem, ibid.*, 1965, **37**, 1556.
4. N. Nakamura and E. Sekido, *Talanta*, 1970, **17**, 515.
5. D. Kealey and H. Freiser, *ibid.*, 1966, **13**, 1381.
6. Yu. A. Bankovskii, L. M. Chera and A. F. Ievin'sh, *Zh. Analit. Khim.*, 1963, **18**, 668.
7. Y. Mido and E. Sekido, *Bull. Chem. Soc. Japan*, 1971, **44**, 2127.

Talanta, 1972, Vol. 19, pp. 647 to 655. Pergamon Press. Printed in Northern Ireland

IMPROVED SYNTHESIS AND STABILITY OF 8-SELENOQUINOLINE AND ITS SODIUM SALT AS ORGANIC REAGENTS

EIICHI SEKIDO and ISAMU FUJIWARA
Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan

(*Received* 18 *June* 1971. *Accepted* 14 *July* 1971)

Summary—The synthesis of 8-selenoquinoline and its sodium salt has been improved by optimization of each process. The stability of the reagents in air and nitrogen has been examined and correlated with the drying method. Both 8-selenoquinoline and its sodium salt can exist as the monohydrate. It was found that the sodium salt of 8-selenoquinoline monohydrate is best as the weighing form of the reagent and that it can be kept stable under nitrogen in a vessel containing silica gel.

8-SELENOQUINOLINE (8-quinolineselenol), so-called selenoxine, was synthesized by Sekido, Fernando and Freiser,[1] and the properties of this reagent and some of its metal chelates were studied.[2–4] Because of the poor yield and its instability in air, however, further studies appeared necessary.

Hitherto, 8-selenoquinoline has been synthesized according to scheme I. The diazotization of 8-aminoquinoline proceeds successfully in mineral acid but the resulting diazonium salt solution does not necessarily react smoothly with potassium selenocyanate; consequently the yield of 8-selenoquinoline or 8,8′-diquinolyldiselenide is usually poor. 8-Selenoquinoline is so unstable in air that it is necessary to take care in storing it, and on the other hand 8,8′-diquinolyldiselenide must be reduced just before use.

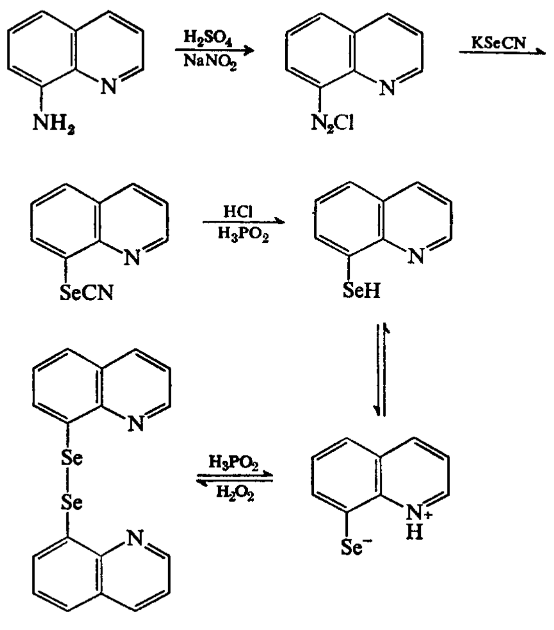
This paper deals with the improved synthesis of 8-selenoquinoline and the stability of 8-selenoquinoline and its sodium salt as a function of the drying method used.

EXPERIMENTAL

Synthesis of 8-selenoquinoline and its sodium salt

8-Selenocyanatoquinoline. Pure 8-aminoquinoline (15 g, 0·105 mole) prepared from 8-hydroxyquinoline,[3] is dissolved in 48% hydrobromic acid (78 ml, 0·50 mole) and water (200 ml). Into the solution cooled to 0°, 10% sodium nitrite solution is dropped with stirring. A colour change from red to yellow-green indicates the end of the diazotization. The excess of nitrite is destroyed by addition of 2*M* sulphamic acid until evolution of nitrogen ceases. The diazonium solution is neutralized with solid sodium acetate to pH 1·5–2·0, in an ice-bath. Then 15% potassium selenocyanate solution (100 ml, 0·104 mole) is added slowly during one hour, at below 5°. The bulky yellow-brown product is formed as a suspension and nitrogen is evolved. To complete the reaction, the solution is stirred for 30 min at below 5° and then for several hours at room temperature (in a fume-cupboard). The solution is adjusted to pH 8·0 with 12*M* sodium hydroxide and the precipitate filtered off. If 1% hydrogen peroxide solution is added to the filtrate, a little yellow-brown precipitate may be formed. This precipitate, probably impure 8,8′-diquinolyldiselenide, is added to the 8-selenocyanatoquinoline in the following procedure. 8-Selenocyanatoquinoline can be recrystallized from 50% v/v aqueous methanol (to give yellow-brown needles, m.p. 74–75°), but as it is an evil-smelling compound and the recrystallization is difficult, the crude compound is used in the following procedure.

8,8′-Diquinolyldiselenide. The crude 8-selenocyanatoquinoline (10 g, 0·043 mole) is dissolved in 6*M* hydrochloric acid (50 ml) and 50% hypophosphorous acid (10 ml) and the resulting solution is warmed for about 15 min on a water-bath. The colour changes gradually from yellow to red, which indicates the formation of 8-selenoquinoline by hydrolysis of 8-selenocyanatoquinoline. After cooling in an ice-bath, the impurity is filtered off (in a fume-cupboard, because hydrogen cyanide gas may



Scheme I

be produced). The 8-selenoquinoline in acid solution is neutralized with 5*M* sodium hydroxide in an ice-bath while nitrogen is bubbled through the solution. The colour changes to red-violet in weakly acidic or neutral solution and then to yellow in alkaline solution. The alkaline solution of 8-selenoquinoline is rapidly filtered under nitrogen to remove the impurities. When 1% hydrogen peroxide solution is added to the filtrate, a white precipitate of 8,8′-diquinolyldiselenide forms rapidly. The precipitate is filtered off, washed with water and dried *in vacuo* at room temperature. It is purified by dissolving it in hydrochloric and hypophosphorous acids and repeating the above-mentioned procedure. Yield, 40% (from 8-aminoquinoline); fine white crystals, m.p. 205° (lit.,[1] 205–206°). Calculated for $C_{18}H_{12}N_2Se_2$: C, 52·19%; H, 2·92%; N, 6·76%. Found: C, 52·6%; H, 3·0%; N, 7·3%.

8-Selenoquinoline. Purified 8,8′-diquinolyldiselenide (15 g) is dissolved in as little 6*M* hydrochloric acid as possible and 50% hypophosphorous acid (5 ml). The colour changes from yellow to red, which indicates the formation of 8-selenoquinoline. To complete the reduction the solution is warmed on a water-bath for about 10 min. It is not favourable to heat at high temperature and for a long time. After cooling, the solution is filtered if necessary, put in an ice-bath, and kept under nitrogen while 12*M* sodium hydroxide is added dropwise. The red solution becomes deep violet-red and then a precipitate forms, which redissolves on further addition of sodium hydroxide, to give a yellow solution, which is rapidly filtered if necessary. Then 2*M* hydrochloric acid is carefully added until the pH reaches 4, and dark red-brown needles precipitate. The precipitate is rapidly filtered off under nitrogen and washed with oxygen-free cold water. The 8-selenoquinoline is dried and kept in a desiccator containing silica gel and filled with nitrogen. More product can be obtained by repeating the procedure with the filtrate and washings. Yield, 52%; red-brown needles, m.p. not measurable (oxidation to 8,8′-diquinolyldiselenide). Calculated for C_9H_7NSe: C, 51·94%; H, 3·39%. Found: C, 51·7%; H, 3·6%.

Sodium salt of 8-selenoquinoline. When 12*M* sodium hydroxide is added to an acidic solution of 8-selenoquinoline, in an ice-bath under nitrogen, the yellow sodium salt of 8-selenoquinoline is precipitated. After filtration, the sodium salt is dried and recrystallized from 95% ethanol at least thrice. The amount of water of crystallization depends on the method of drying. Drying and storage in a desiccator containing silica gel and filled with nitrogen yields the monohydrate. Yield, 21·0% (from 8,8′-diquinolyldiselenide); yellow crystals, Calculated for $C_9H_8NOSeNa$: C, 43·57%; H, 3·25%. Found: C, 43·3%; H, 3·6%.

When the salt is dried *in vacuo* at 120°, the anhydride is obtained. Yellow crystals; Calculated for C_9H_6NSeNa: C, 46·98%; H, 2·63%; N, 6·09%. Found: C, 46·7%; H, 2·9%; N, 5·9%.

Other reagents

8-Mercaptoquinoline was prepared by the method of Kealey and Freiser[5] and its sodium salt by the method of Nakamura and Sekido.[4]

Apparatus

Drying. Vacuum desiccators containing silica gel or calcium chloride as desiccant were used for drying at room temperature and an electric oven under reduced pressure for drying by heating.

RESULTS AND DISCUSSION

Synthesis of 8-selenoquinoline

The improvements in the synthesis of 8-selenoquinoline are summarized in Table I.

TABLE I.—IMPROVEMENTS OF THE SYNTHESIS OF 8-SELENOQUINOLINE COMPARED WITH THE CONVENTIONAL METHOD

Reaction parameter	This method	Conventional method[1]
Acidity of diazotization	Mineral acids (HCl, HBr or H_2SO_4) 0·25M	H_2SO_4, 0·1M
Neutralization of diazonium salt solution	Addition of solid sodium acetate	Addition of 5M sodium hydroxide
Acidity of diazonium salt solution and KSeCN solution	pH 1·5–2·5	pH 7·0
Order of addition	Addition of KSeCN to diazonium salt solution	Addition of diazonium salt solution to KSeCN solution
Temperature and time of the reaction	30 min in an ice-bath and then 60 min at room temperature	30 min in an ice-bath
Yield of 8,8′-diquinolyldiselenide from 8-aminoquinoline	40%	12% (Maximum)

Effect of acidity on the diazotization of 8-aminoquinoline. It was found that the diazotization proceeds in hydrochloric or hydrobromic acid as well as in sulphuric acid and that at least 5 equivalents of acid per equivalent of 8-aminoquinoline are needed for smooth diazotization.

Neutralization of diazonium salt of 8-aminoquinoline. When 5M sodium hydroxide is used for neutralization to pH 1·5–2·5, higher pH values may be attained locally. In addition, heating by the exothermic reaction might accelerate decomposition of the diazonium salt. Use of more dilute sodium hydroxide solution makes the volume too large, and causes difficulty later. Addition of solid sodium acetate eliminates these disadvantages.

Acidity of the diazonium salt solution and the potassium selenocyanate solution. Potassium selenocyanate decomposes in acid solution to yield colloidal red selenium.

The rate of decomposition as a function of pH is as follows:

pH	below 1	1·0	2·0	4·0	5·0	7·0
Decomposition time, *min*	instantly	2	5–6	5–6	10	no change

The decomposition is accelerated by increase in temperature.

Although the diazonium salt of 8-aminoquinoline is stable in strongly acidic solution, it decomposes at higher pH. The yield of 8,8′-diquinolyldisulphide by reaction of the diazonium salt with thiourea was used to monitor the effect of pH on decomposition of the diazonium salt (the rate of reaction of the urea increases with pH, so an inverse relationship of yield to pH indicates faster decomposition as the pH is increased):

pH	−0·4	1·0	2·0	4·0	5·0	7·0
Yield, %	50	40	32	19	7	9

The best compromise between decomposition of the diazonium salt and of potassium selenocyanate was to use a pH of 1·5–2·5.

Order of addition of the diazonium salt and selenocyanate. If the neutralized diazonium salt solution is added to the selenocyanate solution,[1] the product becomes very tarry and difficult to remove. The reverse order of addition was found to give a readily filterable yellow-brown precipitate.

Drying conditions. The effect of varying the drying conditions is shown in Table II.

TABLE II.—WATER CONTENT AND COLOUR OF 8-SELENOQUINOLINE AND ITS SODIUM SALT WHEN THESE ARE DRIED UNDER VARIOUS CONDITIONS

		Drying condition					
No.	Substance	Desiccant	Atmosphere	Temp., °*C*	Time, *hr*	Water content,* %	Colour
1	8-SQ†	silica gel	nitrogen	20–25	24	8·2	red
2	8-SQ†	silica gel	nitrogen	20–25	48	0	red-brown
3	8-SQ†	silica gel	vacuum (0·1 μbar)	20–25	24	0	red-brown
4	8-SQ†	$CaCl_2$	nitrogen	20–25	48	0	red-brown
5	8-SQ-Na‡	silica gel	vacuum (0·1 μbar)	20–25	24	6·7	yellow
6	8-SQ-Na‡	silica gel	(0·1 μbar)	20–25	48	7·6	yellow
7	8-SQ-Na‡	silica gel	(0·1 μbar)	20–25	7 days	7·2	yellow
8	8-SQ-Na‡	silica gel	25–40 mbar	20–25	48	7·8	yellow
9	8-SQ-Na‡	no	vacuum (0·1 μbar)	120	1–6	0	orange

* Average value of at least 5 results. Range ±0·5%. One molecule of water of crystallization corresponds to 8·0% H_2O for 8-SQ and 7·3% for 8-SQ-Na.

† 8-SQ: 8-selenoquinoline.

‡ 8-SQ-Na: sodium salt of 8-selenoquinoline.

Experiments 1–4 show that 8-selenoquinoline easily loses its water of crystallization. In contrast, the sodium salt exists as the monohydrate over a fairly wide range of drying conditions. The anhydrous salt is so hygroscopic that it must be kept in a desiccator containing phosphorus pentoxide.

Thermal stability of 8-selenoquinoline and its sodium salt

8-Selenoquinoline, especially its monohydrate, is easily oxidized in air to 8,8′-diquinolyldiselenide. Therefore, its thermal stability was examined in nitrogen as well as in air. Thermogravimetry of 8-selenoquinoline monohydrate in air (curve *A* in Fig. 1) shows loss of the water at a temperature of 51° or lower, accompanied by a colour change to red-brown at 50–51°. These facts may support the hypothesis that the water is not adsorbed by 8-selenoquinoline but weakly bound to it as shown in structure **I**. Bankovskii, Chera and Ievin'sh[6] proposed structure **II** for 8-mercaptoquinoline dihydrate. Considering the difference in the acid dissociation constants[1] of —SH in 8-mercaptoquinoline and —SeH for 8-selenoquinoline (in other words, the difference of electronegativities for sulphur and selenium) the S· · ·H bond in **II** may be stronger than the Se· · ·H bond in **I**.

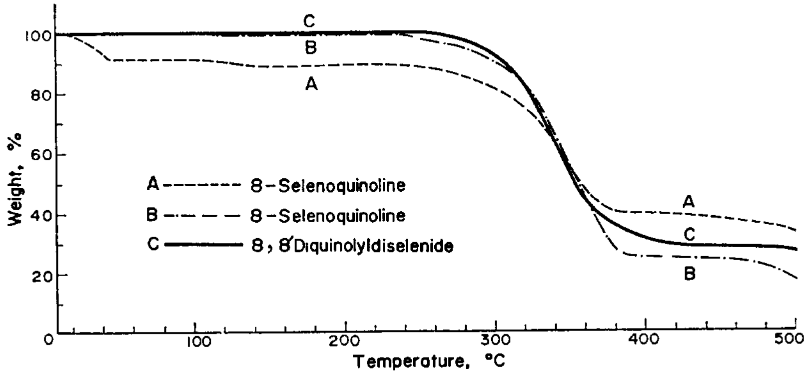
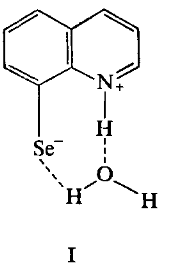
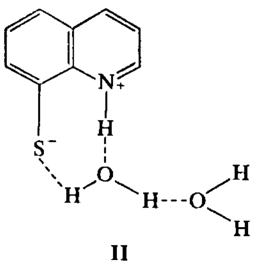


FIG. 1.—Thermogravimetric curves of 8-selenoquinoline and 8,8′-diquinolyldiselenide in air.



I



II

Therefore, the temperature of dehydration for 8-mercaptoquinoline (58–59°) should be higher than that for 8-selenoquinoline (51°). In the case of 8-mercaptoquinoline, the second water molecule may be weakly connected *via* a hydrogen bond to the cyclically bound water molecule.

The anhydride (curve *A* above 50° and curve *B* in Fig. 1) changes to 8,8′-diquinolyldiselenide by 140° (*cf.* curve *C* in Fig. 1). The oxidation of 8-selenoquinoline is also confirmed by the identity or the infrared spectra of the product from 8-selenoquinoline heated to 180–190° and of 8,8′-diquinolyldiselenide. The differential thermal analysis (DTA) and thermogravimetric curves of 8-selenoquinoline under nitrogen (curves *A* and *A'* in Fig. 2) are different from those of 8,8'-diquinolyldiselenide (curves *C* and *C'*). The peak at 204° on curve *C* corresponds to melting of 8,8'-diquinolyldiselenide and that at 360° to decomposition of the quinoline nucleus.

8-Selenoquinoline is completely oxidized to 8,8'-diquinolyldiselenide after 3 hr in air. This oxidation is confirmed by the disappearance of the infrared absorption band at 2925 cm^{-1} (N–H stretching vibration) and by the agreement with the infrared spectrum of 8,8'-diquinolyldiselenide. Anhydrous 8-selenoquinoline is stable for at least three weeks when stored under nitrogen in a vessel containing silica gel.

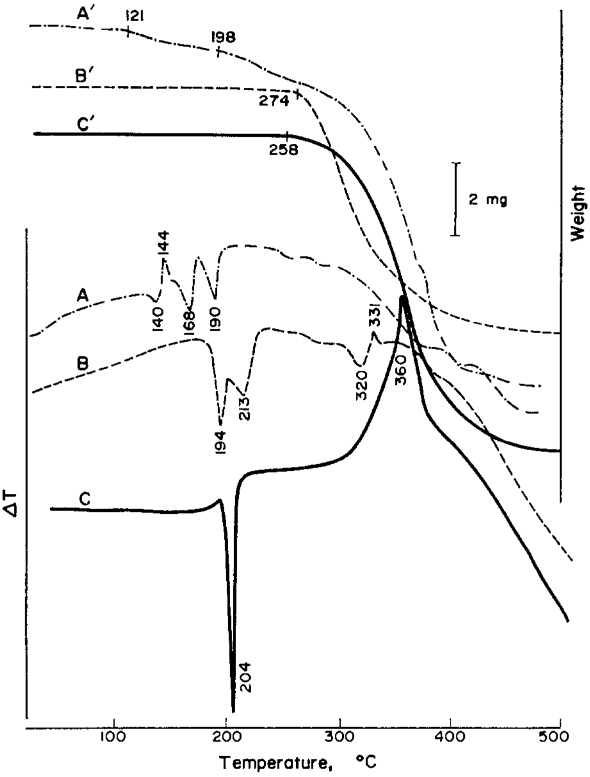
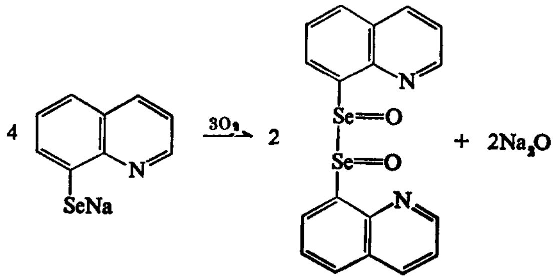


FIG. 2.—Differential thermal curves (A, B and C) and thermogravimetric curves (A', B' and C') of the reagents in nitrogen gas. A and A': 8-selenoquinoline; B and B': 8,8'-diquinolyldisulphide; C and C': 8,8'-diquinolyldiselenide.

Thermogravimetric curves for the sodium salt of 8-selenoquinoline in nitrogen and in air are shown in Fig. 3. The water is all lost between 78 and 106° (curve *A*). The anhydride increases in weight by 10% over the temperature range 160–190° if heated in air (curves *A* and *B*) but not if heated in nitrogen or carbon dioxide (curve *C*). A similar phenomenon occurs with the sodium salt of 8-mercaptoquinoline,[7] and not for 8-selenoquinoline or 8,8'-diquinolyldiselenide. It is assumed that the sodium salt of 8-selenoquinoline is oxidized by air. Oxidation according to the reaction below gives a theoretical weight increase of 10·4% (experimental value, 10·0%).



The DTA curves for the sodium salts of 8-selenoquinoline monohydrate and 8-mercaptoquinoline dihydrate are shown in Fig. 4; for both there is a large endothermic peak at about 120°, which corresponds to loss of the water. The rest of the decomposition is rather complex. The bond strength between the water and the organic molecule is presumably almost the same for both compounds. The O–H stretching vibration in the infrared spectra for both compounds exists at almost the same position, 3277 cm^{-1} for the 8-selenoquinoline salt and 3200–3300 cm^{-1} for that of 8-mercaptoquinoline, the first being relatively sharp and the other broad (Fig. 5). These facts suggest that the structures may be III and IV respectively.

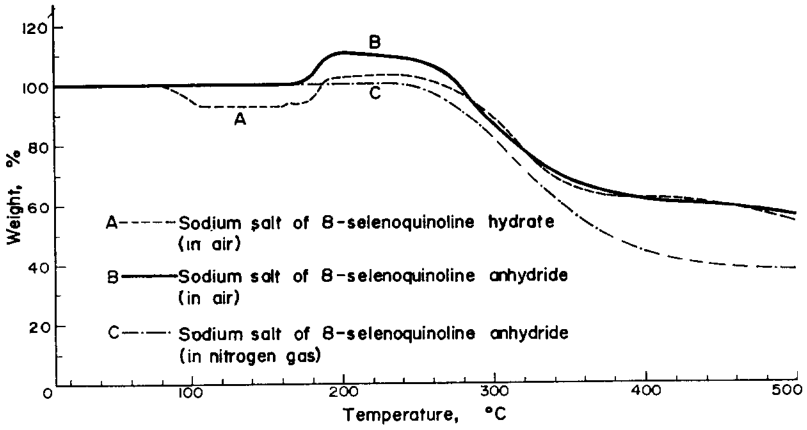
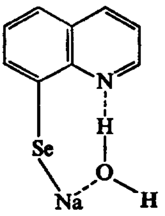
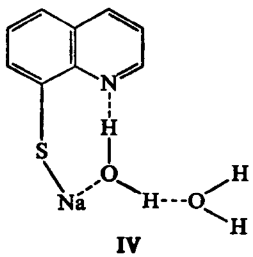


FIG. 3.—Thermogravimetric curves of the sodium salt of 8-selenoquinoline in air and nitrogen.



III



IV

That the dehydration temperature of the sodium salts is higher than that of the 8-seleno- or 8-mercaptoquinoline may be attributed to the bond between the sodium

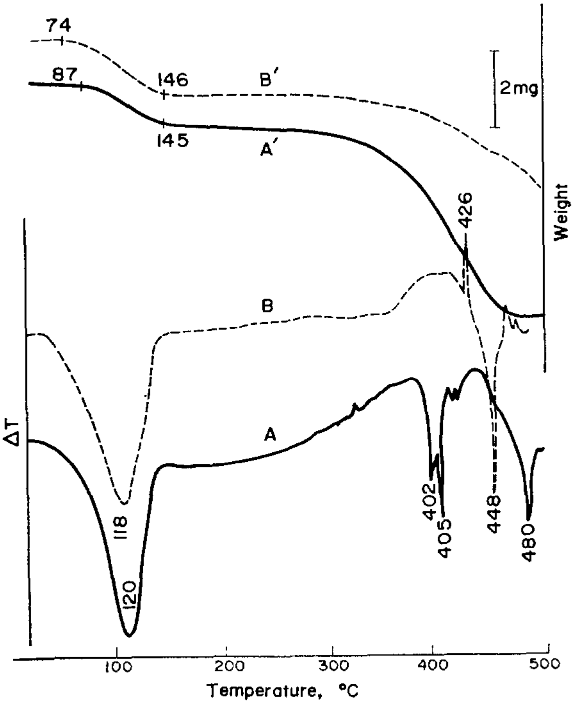


FIG. 4.—Differential thermal curves (A and B) and thermogravimetric curves (A' and B') of the reagents in nitrogen gas. A and A': sodium salt of 8-selenoquinoline; B and B': sodium salt of 8-mercaptoquinoline.

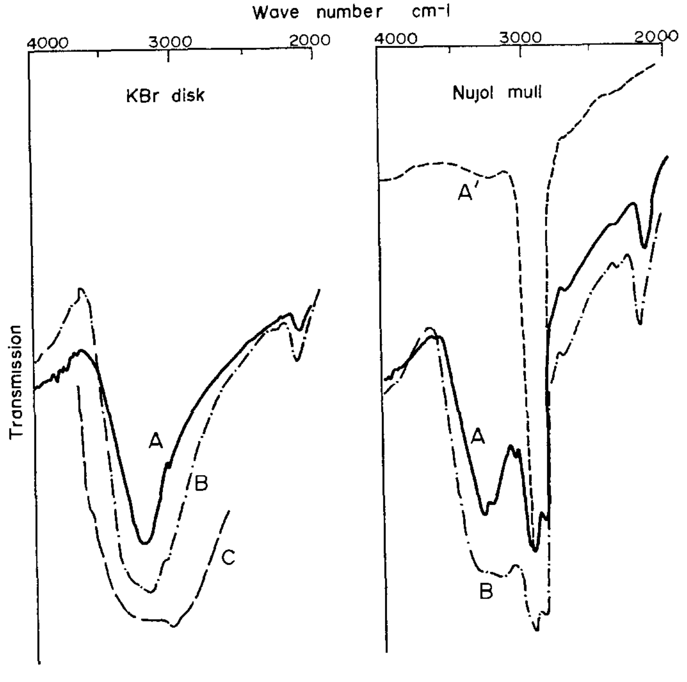


FIG. 5.—Infrared spectra of sodium salt of the reagents in the region of 4000–2000 cm^{-1}. A: 8-selenoquinoline monohydrate; *A'*: its anhydride; B: 8-mercaptoquinoline dihydrate; C: 8-hydroxyquinoline hydrate.

atom and the oxygen atom of water being stronger than that between the oxygen atom and the selenium or the sulphur atom. Furthermore, the similar dehydration temperatures for the sodium salts suggest that one water molecule exists between the sodium atom and the nitrogen atom of the quinoline nucleus in both. The second water molecule of the dihydrate, being bound to the cyclically bound water molecule by a hydrogen bond, will broaden the O—H stretching vibration band.

The temperature of incipient decomposition of the sodium salt of 8-selenoquinoline is lower than that for 8-mercaptoquinoline salt; the S—Na bond may be stronger than the Se—Na bond.

The anhydrous sodium salt of 8-selenoquinoline is so hygroscopic that it abstracts water from silica gel in a desiccator. It is stable if kept in a nitrogen atmosphere over phosphorus pentoxide in a desiccator, but over P_2O_5 in a vacuum it changes gradually into a red-brown compound. The sodium salt monohydrate is the best storage form, being stable for at least 2½ months in a nitrogen atmosphere in a desiccator containing silica gel.

Zusammenfassung—Die Synthese von 8-Selenochinolin und seines Natriumsalzes wurde durch Optimierung jeder Stufe verbessert. Die Stabilität der Reagentien an Luft und Stickstoff wurde geprüft und mit der Trocknungsmethode in Zusammenhand gebracht. Sowohl 8-Selenochinolin als auch sein Natriumsalz können als Monohydrat existieren. Es wurde gefunden, daß das Natriumsalz von 8-Selenochinolin-Monohydrat die beste Wägeform des Reagens darstellt und daß es unter Stickstoff in einem Silicagel enthaltenden Gefäß stabilisiert werden kann.

Résumé—On a amélioré la synthèse de la 8-sélénoquinoléine et de son sel de sodium en optimalisant chaque opération. On a examiné la stabilité des réactifs à l'air et sous azote et on l'a rattachée à la méthode de séchage. La 8-sélénoquinoléine et son sel de sodium peuvent exister à l'état de monohydrate. On a trouvé que le monohydrate du sel de sodium de la 8-sélénoquinoléine est la meilleure forme du réactif pour la pesée et qu'il peut être conservé de manière stable sous azote dans un récipient contenant du gel de silice.

REFERENCES

1. E. Sekido, Q. Fernando and H. Freiser, *Anal. Chem.*, 1964, **36**, 1768.
2. *Idem, ibid.*, 1963, **35**, 1550.
3. *Idem, ibid.*, 1965, **37**, 1556.
4. N. Nakamura and E. Sekido, *Talanta*, 1970, **17**, 515.
5. D. Kealey and H. Freiser, *ibid.*, 1966, **13**, 1381.
6. Yu. A. Bankovskii, L. M. Chera and A. F. Ievin'sh, *Zh. Analit. Khim.*, 1963, **18**, 668.
7. Y. Mido and E. Sekido, *Bull. Chem. Soc. Japan*, 1971, **44**, 2127.

Talanta, 1972, Vol. 19, pp. 657 to 668. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF PLUTONIUM BY TWO-STEP FLOW-COULOMETRY AT THE COLUMN ELECTRODE

SORIN KIHARA, TADASHI YAMAMOTO and KENJI MOTOJIMA
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun,
Ibaraki-ken, Japan

and

TAITIRO FUJINAGA
Department of Chemistry, Faculty of Science, Kyoto University,
Kitashirakawa, Sakyo-ku, Kyoto, Japan

(*Received* 12 *November* 1970. *Revised* 25 *April* 1971. *Accepted* 28 *June* 1971)

Summary—A two-step flow-coulometry method has been developed for rapid determination of elements (plutonium, iron, *etc*) which exist in various oxidation states in solution, and applied to the determination of plutonium in 0·5*M* sulphuric acid medium. The first-step column electrode potential is fixed at between +0·10 and +0·35 V *vs.* Ag–AgCl, and all plutonium ions are reduced to Pu(III). The second-step column electrode potential is fixed at +0·75 V *vs.* Ag–AgCl, and Pu(III) which flows from the first column electrode is oxidized to Pu(IV). The quantity of plutonium is determined from the number of coulombs used in the oxidation. It is possible to eliminate interference by diverse ions by electroanalysis at the first column electrode. About a 10-μl sample is necessary and the electrolysis for determination is finished in 1 min.

IT IS WELL KNOWN that plutonium has several oxidation states such as PuO_2^{2+}, PuO_2^{+}, Pu^{4+} and Pu^{3+} in aqueous solution (Pu^{4+} and Pu^{3+} are more stable than the others), and it is difficult to convert them into a single oxidation state by simple chemical procedures. Since plutonium is strongly poisonous, care must be taken in its handling (*e.g.* glove-box operation) and complex procedures are not practical in plutonium analyses.

In this work, the flow-coulometric method[1] has been applied to the determination of plutonium, and a two-step flow-coulometry method has been developed. Micro-amounts of plutonium can be determined precisely by this simple procedure. Plutonium solution (5–50 μl) is passed through the first-step column electrode, which is controlled at a proper potential in order to convert all plutonium into Pu^{3+} ions. The Pu^{3+} ions are passed through the second-step column electrode immediately; here, the working electrode potential is controlled so as to complete the electrode reaction:

$$\mathrm{Pu(III)} - e = \mathrm{Pu(IV)}.$$

The amount of plutonium is then obtained from the integration of the electrolytic current (number of coulombs) at the second-step column electrode:

$$\mathrm{Pu\ (mole)} = \frac{1}{96500}\int_0^\infty i\,\mathrm{d}t$$

where i denotes the oxidation current (A) at time t (sec). The procedure is rapid, and only one minute is required for the whole procedure, including sample injection, valency control at the first-step column electrode and the recording of an electrolytic current at the second-step column electrode. Furthermore, diverse ions which interfere with the determination of plutonium are eliminated at the first-step column electrode by reduction or oxidation.

In the determination of plutonium by electrochemical methods such as potentiometry,[2] coulometry,[3] polarography[4] and amperometry,[5] the oxidation states must be controlled just before the determination. In general, this behaviour of plutonium is a serious source of error in the micro-determination of plutonium. Two-step flow-coulometry, however, will easily be applicable to automatic determination of plutonium in remotely-controlled processes.

EXPERIMENTAL

Reagents

Plutonium. Plutonium metal from Nuclear Materials and Equipment Corporation, U.S.A. (isotopic composition; ^{239}Pu 91·3, ^{240}Pu 7·81, ^{241}Pu 0·85, ^{242}Pu 0·04 atom %) was dissolved in 0·5*M* sulphuric acid after electro-refining and weighing. Plutonium in this solution was expected to be present as a mixture of Pu^{3+}, Pu^{4+} and a small amount of PuO_2^{2+}.

Uranium. Uranium oxide (U_3O_8; Johnson Matthey Co., Ltd.) was dissolved in 6*M* nitric acid and the solution evaporated nearly to dryness. Then the residue was dissolved with small amounts of 0·5*M* sulphuric acid and evaporated almost to dryness. This procedure was repeated three times. The final sulphate solution was prepared by dissolving the residue in 0·5*M* sulphuric acid solution. Uranium in this solution was expected to be present as UO_2^{2+}.

All other reagents used were of extra-pure grade.

Apparatus

The electrolytic cell for two-step flow-coulometry is shown in Fig. 1 and is essentially the same as that described previously[6] except that two column electrodes are used, the distance between them being minimized, and the dispersion of a sample within the carrier solution being kept as small as possible. The glassy carbon counter electrode lasts longer than the silver one used in the previous work.[1] The glassy carbon counter electrodes, however, are not practical in the potential range where electrolysis of the counter electrode solution (saturated potassium chloride solution) takes place markedly. Saturated potassium chloride solution is more suitable for the counter electrode solution than is 0·5*M* sulphuric acid because the solubility of chlorine generated by anodic reaction in saturated potassium chloride solution is greater than that of oxygen generated by anodic reaction in 0·5*M* sulphuric acid.

The glassy carbon working electrode is pretreated as already described. The reference electrode is a saturated KCl–AgCl/Ag electrode (SSE).

Recommended procedure for the determination of plutonium

Pure nitrogen gas is passed through the supporting electrolyte (0·5*M* sulphuric acid) and plutonium sample solution. The supporting electrolyte is passed through the flow-coulometric column electrode at a flow-rate of 5 ± 0·5 ml/min, regulated by varying the height of the solution reservoir. The working potential of the first-column electrode (E_1) is adjusted to +0·35 V *vs.* SSE and that of the second-column electrode (E_2) to +0·75 V *vs.* SSE. Then 10–50 μl of plutonium solution are injected into the supporting electrolyte stream. Plutonium is reduced to Pu(III) at E_1 and Pu(III) is oxidized to Pu(IV) at E_2. The current–time curve for oxidation at E_2 is recorded. The amount of plutonium is determined by integrating the current–time curve and converting the quantity of electricity into weight or concentration.

A blank correction is not needed for the determination of more than 1 μg of plutonium. The total time required for the determination of plutonium (sample injection to recording of current–time curve) is 10–40 sec, depending on the plutonium concentration.

RESULTS AND DISCUSSION

Preliminary studies using the Fe(II)/Fe(III) *couple*

Preliminary studies were made with the Fe(II)/Fe(III) couple as a simple system which has only two oxidation states in aqueous solution. The oxidation-reduction

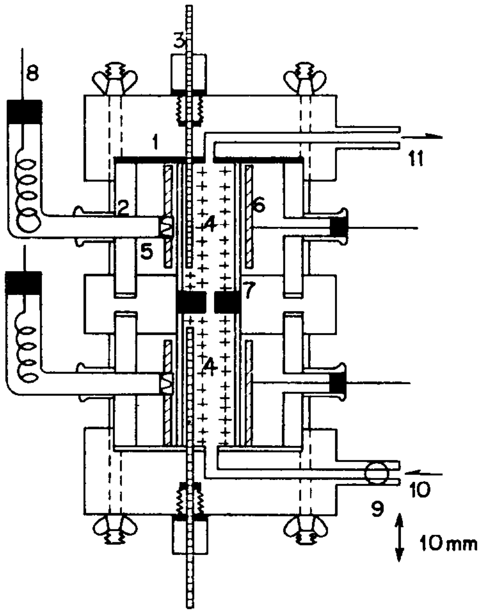


Fig. 1.—Electrolytic cell.
(1) Teflon (2) Glass cylinder
(3) Glassy carbon lead
(4) Glassy carbon grains (working electrode)
(5) Saturated KCl solution
(6) Glassy carbon cylinder (counter electrode)
(7) Porcelain cylinder (8) Ag–AgCl reference electrode
(9) Sample inlet (10) Supporting electrolyte inlet
(11) Supporting electrolyte outlet
■ Silicone rubber.

potential of this couple is near that of the Pu(III)/Pu(IV) couple; the formal oxidation-reduction potentials of Fe(II)/Fe(III) and Pu(III)/Pu(IV) are +0·47 and +0·54 V *vs.* SSE, respectively, in 0·5M sulphuric acid at 25°.

The voltage *vs.* quantity of electricity curves (*E–Q* curves), for the Fe(II)/Fe(III) system in 0·5*M* sulphuric acid, are shown in Fig. 2. Ten μl of 0·02*M* Fe(III) in 0·5*M* sulphuric acid were injected into the carrier solution, *i.e.*, the supporting electrolyte of 0·5*M* sulphuric acid, with the potential at the first-step column electrode (E_1) not applied (open circuit). Curve 1 in Fig. 2 shows the reduction reaction from Fe(III) to Fe(II), on changing the working electrode potential at the second-step column electrode (E_2) from +0·70 to 0·00 V *vs.* SSE.

$$\text{Fe(III)} + e \rightarrow \text{Fe(II)} \quad \text{(Curve 1)}$$

Similarly, curve 2 shows the *E–Q* curve for the oxidation reaction:

$$\text{Fe(II)} - e \rightarrow \text{Fe(III)} \quad \text{(Curve 2)}$$

Curve 3 shows the *E–Q* curve for a mixed sample of 0·0094*M* Fe(III) and 0·0106*M* Fe(II) in 0·5*M* sulphuric acid solution.

From these three curves it is found that if E_1 is +0·10 V *vs.* SSE, Fe(III) ions in the sample solution are all reduced to Fe(II), and the quantity of electricity used in this

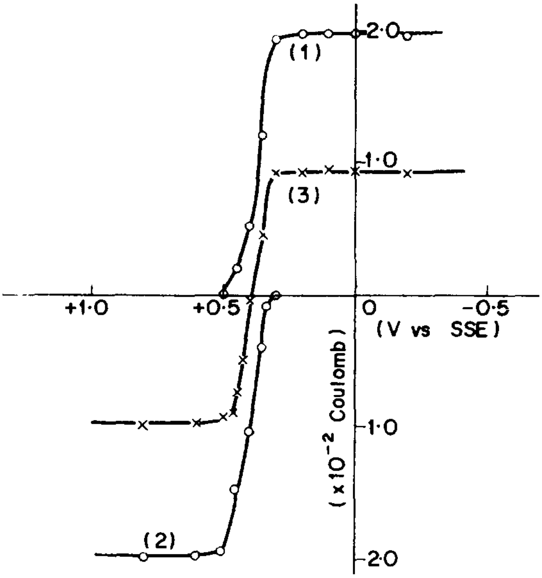


FIG. 2.—Coulomb-potential curves of iron.
Sample: (1) 2×10^{-7} mole Fe^{3+}, (2) 2×10^{-7} mole Fe^{2+}, (3) $0·94 \times 10^{-7}$ mole Fe^{3+}, $1·06 \times 10^{-7}$ mole Fe^{2+}.
Electrolyte: 0·5*M* H_2SO_4.
Flow-rate: 5 ml/min.

reaction is proportional to the amount of Fe(III) ions in the solution, and if E_1 is controlled to +0·65 V *vs.* SSE, Fe(II) ions in the sample solution are all oxidized to Fe(III), and the quantity of electricity for this reaction is proportional to the amount of Fe(II) ions in the solutions.

With the two column electrodes, E_1 is controlled to +0·10 V *vs.* SSE and E_2 to +0·65 V *vs.* SSE. The quantity of electricity used in the second step shows the total amount of iron in the sample solution. The reaction is then Fe(II) — $e \rightarrow$ Fe(III). Similarly, when E_1 is controlled to +0·65 and E_2 to +0·10 V *vs.* SSE, the electrolytic current at the second-step column electrode shows the total amount of iron at the sample solution but the reaction is Fe(III) + $e \rightarrow$ Fe(II). Since both of these reactions correspond to one-electron transfers, the absolute values of these two quantities of electricity are 0·0193 C for the 0·200 μ mole of iron taken.

Figures 3*a* and 3*b* show typical coulometry records. The electrolysis begins at the first-step column electrode 3 sec after sample injection, and after 6 sec it occurs at the second-step column electrode (the arrow shows the time of sample injection). About 50 sec are required to complete the electrolysis. Figure 3*a* shows the case where 10 μl of 0·02*M* Fe(III) are reduced at the first-step column electrode (curve 1) and that in which the Fe(II) reduced is oxidized to Fe(III) again at the second-step column electrode (curve 2). The quantities of electricity for these two electrochemical reactions are similar, and are equal to the theoretical value of 0·0193 C. Figure 3*b* shows 10 μl of sample solution, 0·0106*M* Fe(III) and 0·0094*M* Fe(II), reduced at the first-step electrode (E_1 = +0·10 V *vs.* SSE, curve 3) and then oxidized at the second-step electrode (E_2 = +0·65 V *vs.* SSE, curve 5). Curve 4 corresponds to the oxidation of

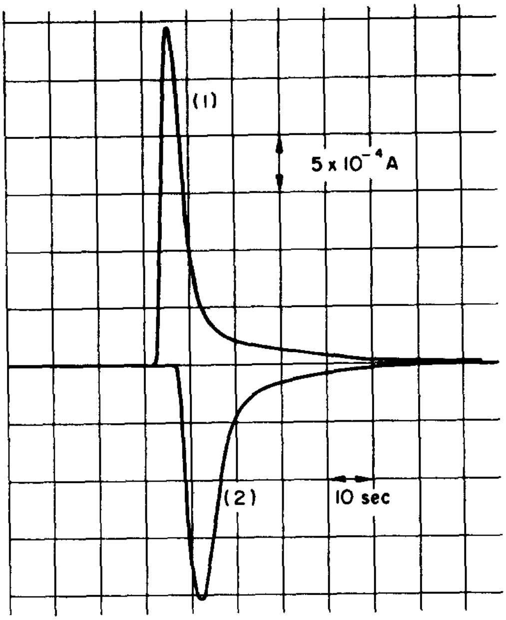


FIG. 3a.—Current-time curve recorded with 10 μl of 2·0 × $10^{-2}M$ Fe(III).
Electrolyte: 0·5M H_2SO_4.
Flow-rate: 5 ml/min.

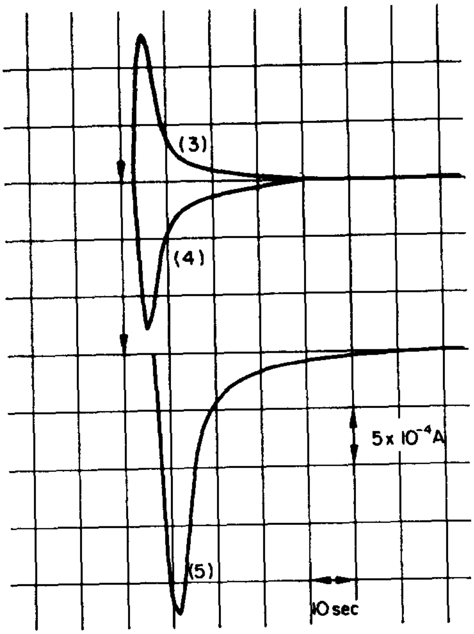


FIG. 3b.—Current-time curve recorded with 10 μl of 1·06 × $10^{-2}M$ Fe(III) + 0·94 × $10^{-2}M$ Fe(II).
Electrolyte: 0·5M H_2SO_4.
Flow-rate: 5 ml/min.

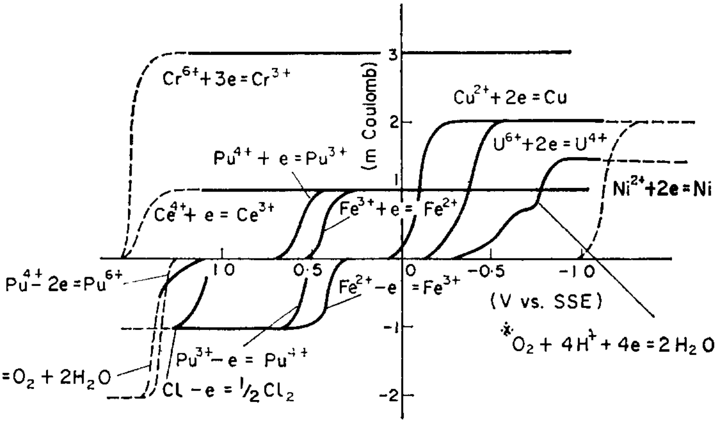


FIG. 4.—Typical coulomb-potential curves of various metal ions at glassy carbon grain column electrode.

Sample: 10^{-8} mole, ·×· 10 μl of air-saturated 0·5*M* H_2SO_4.

Electrolyte: 0·5*M* H_2SO_4.

(Broken lines show oxidation or reduction precedes that of samples.)

the solution at the first-step electrode ($E_1 = +0{\cdot}65$ V *vs.* SSE). The sum of the integrated values of curves 3 and 4 is equal to that of curve 5.

E–Q curves of various ions

The *E–Q* curves for the Cu(II)/Cu, U(VI)/U(IV), $\frac{1}{2}Cl_2/Cl^-$, Ce(IV)/Ce(III), Cr(VI)/Cr(III), Ni(II)/Ni, $\frac{1}{2}O_2/H_2O_2$ and $\frac{1}{2}O_2/OH^-$ reactions are shown in Fig. 4. Ten μl of $10^{-3}M$ solutions of various metal ions, chloride ion and hydrogen peroxide and 10 μl of air-saturated 0·5*M* sulphuric acid, were injected into the carrier solution (0·5*M* sulphuric acid), with E_1 not applied (open circuit) and *E–Q* curves were obtained by changing E_2. The broken lines show estimated *E–Q* curves because the reduction or oxidation reaction of the elements is preceded by that of the solvent. The oxidation states of iron and plutonium samples were adjusted previously by controlled potential electrolysis.

The *E–Q* curve of Cu(II)/Cu in 0·5*M* sulphuric acid is about 0·4 V more negative than that of the Fe(III)/Fe(II) couple, as shown in Fig. 4. Therefore copper ions do not interfere with the determinations of iron mentioned above. If E_1 is controlled to +0·65 V *vs.* SSE and E_2 to —0·25 V *vs.* SSE, the total amount of iron plus copper ions can be obtained. The difference of these two results (at $E_2 = +0{\cdot}10$ V and $E_2 =$ —0·25 V) gives the amount of copper ions. The amounts of iron and copper ions could be determined without mutual interference.

Coulometry of plutonium

Figure 4 shows that the cathodic and anodic reactions of the Pu(III)/Pu(IV) couple are both about 0·1 V more positive than those for the Fe(II)/Fe(III) couple. The *E–Q* curves for plutonium are shown in Fig. 5. Ten μl of $4{\cdot}18 \times 10^{-3}M$ plutonium [Pu(III) and Pu(IV) present] solution were used as the sample. Curve 1 shows the reduction reaction of Pu(IV) to Pu(III) on varying E_2 from +0·80 to —0·20 V *vs.*

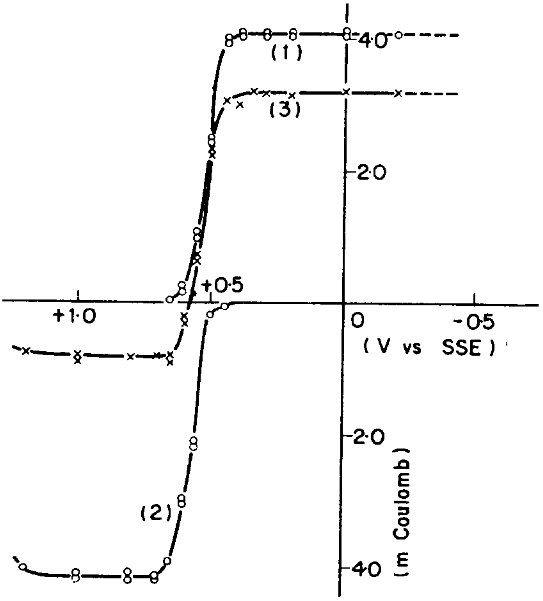


FIG. 5.—Coulomb-potential curves of plutonium.
Sample: 4·18 × 10^{-8} mole Pu.
Electrolyte: 0·5*M* H_2SO_4.
(1) Pu(IV) + *e* = Pu(III).
(2) Pu(III) − *e* = Pu(IV).
(3) Mixture of Pu(III) and Pu(IV).
(The solution was left for five months after dissolution of the plutonium metal.)

SSE. Pu(IV) was produced at the first-step column electrode when potential E_1 was controlled to +0·75 V *vs.* SSE.

$$\mathrm{Pu(IV)} + e \rightarrow \mathrm{Pu(III)} \quad \text{(Curve 1)}$$

Similarly, curve 2 shows the oxidation of Pu(III) to Pu(IV).

$$\mathrm{Pu(III)} - e \rightarrow \mathrm{Pu(IV)} \quad \text{(Curve 2)}$$

Pu(III) was produced at the first-step column electrode, the potential of which was controlled to +0·10 V *vs.* SSE. Curve 3 shows the oxidation and reduction reactions for the mixed solution of Pu(III) and Pu(IV) (a solution which had been left for five months after dissolution of the plutonium metal in 0·5*M* sulphuric acid) when E_1 is not applied (open circuit). It is found from curve 3 that the ratio of Pu(IV) to Pu(III) in this solution is nearly 3:1. In this connection, it is confirmed by comparing curve 3 with curve 2 in Fig. 5, that the presence of Pu(VI) is negligibly small in 0·5*M* sulphuric acid. The sum of the quantity of electricity (Q_3) for reduction at +0·35 V and oxidation at +0·75 V, in curve 3, is nearly equal to the quantity of electricity (Q_2) at +0·75 V in curve 2. If Pu(VI) is present, Q_3 should be larger than Q_2 because, at +0·35 V, Pu(VI) should be reduced to Pu(III) and hence a three-electron change should be involved. After controlled potential electrolysis at +0·75 V at a glassy carbon working electrode, the quantity of electricity used at +0·35 V is nearly equal to Q_2. Therefore, it is considered that the oxidation state of plutonium is Pu(IV) after

TABLE I.—DETERMINATION OF PLUTONIUM

Pu taken	*mmole* taken	Coulombs, calculated	Coulombs, found	Pu found, %
1·03 mg/ml 50 μl	215	$2·08 \times 10^{-2}$	$2·04 \times 10^{-2}$	98·1
			2·07	99·5
			2·06	99·0
			2·01	96·7
			2·04	98·1
515 μg/ml 50 μl	108	$1·04 \times 10^{-2}$	$1·05 \times 10^{-2}$	100·9
			1·03	99·0
			1·03	99·0
			1·04	99·6
			1·05	100·9
51·5 μg/ml 50 μl	10·8	$1·04 \times 10^{-3}$	$1·07 \times 10^{-3}$	102·8
			1·04	99·6
			1·05	100·9
			1·03	98·9
			1·05	100·9
10·3 μg/ml 50 μl	2·2	$2·08 \times 10^{-4}$	$2·20 \times 10^{-4}$	105·9
			2·07	99·6
			2·02	97·1
			2·15	103·5
			2·05	98·5
5·0 μg/ml 20 μl	0·42	$4·02 \times 10^{-5}$	$3·97 \times 10^{-5}$	98·7
			3·94	98·0
			4·07	101·1
			3·93	97·8
			3·92	97·5

Potentials; first column +0·35 V *vs.* SSE, second column +0·75 V *vs.* SSE.
Electrolyte; 0·5*M* H_2SO_4.
Flow-rate; 5 ml/min.

electrolysis at +0·75 V. The reason why Pu(VI) generated by the disproportionation reaction of Pu(IV) disappears is not clear, but it can be considered that the reduction of Pu(VI) by hydrogen peroxide[7] or α-ray direct reduction[8] and the enhanced complex-forming power of Pu(IV) with sulphate make Pu(VI) unstable. Hydrogen peroxide is generated by radiolysis of water[7] or reduction of dissolved oxygen by Pu(III).[9]

The results of the determination of plutonium by a method based on the information presented in Fig. 5 are summarized in Table I. It is seen that 0·1 μg (0·42 *p* mole) and above of plutonium can be determined within ±3%. This error may be due to an error in sampling and to the current integration procedure.

Elimination of interference by other ions in the determination of plutonium

From Fig. 4, when reducible substances co-exist in a potential range higher than +0·75 V *vs.* SSE, it is seen that plutonium can be determined by the second-step column electrode if $E_1 = +0·75$ and $E_2 = +0·35$ V *vs.* SSE. Similarly, when oxidizable substances co-exist in a potential range lower than +0·35 V *vs.* SSE, plutonium can be determined by the second-step column electrode if $E_1 = +0·35$ and $E_2 = +0·75$ V *vs.* SSE. The results of determination of diverse ions alone, and of plutonium in co-existence with these ions, are summarized in Table II, which shows that plutonium can be determined without interference by these elements.

TABLE II.—EFFECT OF DIVERSE IONS ON DETERMINATION OF PLUTONIUM

Element taken,	*p mole*	Electrode potential (*V vs.* SSE) first	second	Apparent Pu found (*p mole*)	%
Ce	642	+0·75	0·00	4·4 3·2 3·2	
Cr	1600	+0·75	0·00	~0	
Cu	400	+0·75	0·00	2·6 2·0 2·6	
		+0·75	0·00	~0	
		0·00	+0·75	~0	
Ni	800	+0·75	0·00	~0	
		0·00	+0·75	~0	
U	398	+0·75	0·00	~0	
		0·00	+0·75	~0	
Cl	800	+0·75	0·00	~0	
Pu	41·8	+0·75	+0·10	41·2	101·2
+ Ce	64·2			40·7	99·9
Cr	160			41·9	102·7
Cu	40·1				
Ni	80·0				
U	39·8				
Cl	80·0				

Electrolyte; 0·5M H_2SO_4.
Flow-rate; 5 ml/min.

Coulometric determination of plutonium in the presence of iron

As seen in Fig. 4, the oxidation-reduction potential of the Pu(III)/Pu(IV) couple is similar to that of the Fe(II)/Fe(III) couple, and it is difficult to determine plutonium in the presence of iron by ordinary electrolysis.

The E–Q curves of plutonium (curves 1, 1′) and iron (curves 2, 2′) are shown in Fig. 6. Curves 1 and 2 show the reduction reactions of Pu(IV) and Fe(III), respectively, at $E_1 = +0{\cdot}75$ V *vs.* SSE and varying E_2. Curves 1′ and 2′ show the oxidation reactions of Pu(III) and Fe(II), respectively, at $E_1 = +0{\cdot}10$ V *vs.* SSE and varying E_2. The determination of plutonium in the presence of iron was attempted by varying E_2 with E_1 controlled at +0·75 V *vs.* SSE. The results are shown in Table III. The error in determination is minimum at $E_2 = +0{\cdot}45$ V *vs.* SSE. For $E_2 = +0{\cdot}45$ V and $E_1 = +0{\cdot}75$ V *vs.* SSE, the effect of iron on the determination of plutonium is shown in Table IV. Plutonium in the presence of 6% of its weight of iron can be determined with an error of ±3%.

Differential determination of plutonium and uranium by coulometry

The determination of plutonium and uranium in mixtures is often important, especially when mixed oxides or carbides of plutonium and uranium are used as

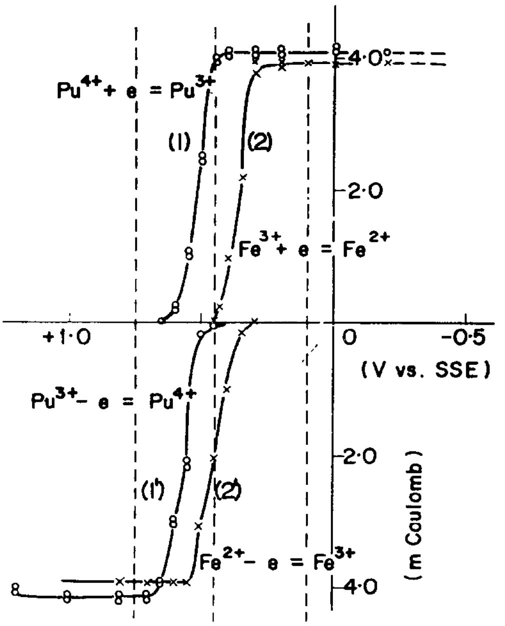


FIG. 6.—Coulomb-potential curves of plutonium and iron.
Sample: Pu 4·18 × 10^{-8} mole, Fe 4·00 × 10^{-8} mole.
Electrolyte: 0·5*M* H_2SO_4.
Flow-rate: 5 ml/min.

TABLE III.—EFFECT OF IRON ON THE DETERMINATION OF PLUTONIUM AT DIFFERENT REDUCTION POTENTIALS

	Second-column potential, *V vs.* SSE			
	+0·500	+0·475	+0·450	+0·425
mC	1·27	1·89	2·20	2·24
found	1·39	1·81	2·21	2·31
	2·41	1·97	2·23	2·30
Theoretical	2·04 mC			

First-column potential; +0·75 V *vs.* SSE.
Electrolyte; 0·5*M* H_2SO_4.
Flow-rate; 5 ml/min.
Sample; 21·1 *p mole* Pu, 20·0 *p mole* Fe.

nuclear fuels. After preliminary studies with plutonium and uranium as described above, a determination procedure for mixed plutonium and uranium oxides has been established. The procedure is as follows.

Determination of the Pu/(Pu + U) *ratio.* The mixed oxide sample (100 mg) is dissolved in 5 ml of 10*M* nitric acid plus 3 drops of 1*M* hydrofluoric acid in 10*M* nitric acid. The nitrate solution is evaporated to near dryness. To the residue are added 10 ml of 0·5*M* sulphuric acid, and the solution is evaporated almost to dryness, and the procedure is repeated three times. The final sample solution is prepared by dissolving the residue in 25 ml of 0·5*M* sulphuric acid, and deaerated by passage of pure nitrogen gas. Ten μl of this solution are taken, and plutonium and uranium determined by two-step flow-coulometry as follows.

Determination of plutonium. Plutonium in the solution is reduced to Pu(III) and uranium is

TABLE IV.—DETERMINATION OF PLUTONIUM IN THE PRESENCE OF IRON

Fe taken, *p mole*	mC found	Pu found (%)
20·0	2·20	107·9
	2·23	109·5
	2·21	108·3
10·0	2·14	104·9
	2·09	102·5
	2·17	106·4
5·00	2·08	102·0
	2·06	101·0
	2·11	103·5

First-column potential; +0·75 V *vs.* SSE.
Second-column potential; +0·45 V *vs.* SSE.
Electrolyte; 0·5*M* H_2SO_4.
Flow-rate; 5 ml/min.
Sample; 21·1 *p mole* Pu (2·04 mC).

TABLE V.—DETERMINATION OF Pu/(Pu + U) RATIO

Sample nominal ratio, %	Pu found, *mg*	U found, *mg*	Pu/(Pu + U), %
25	21·8	65·5	25·0
	30·4	90·7	25·1
	22·1	66·2	25·1
30	33·3	82·2	28·8
	32·8	84·0	28·1
	32·8	80·1	29·0
33	24·3	49·8	32·8
	23·0	47·0	32·9

oxidized to U(VI) at the first-step column electrode (E_1 = +0·10 V). Pu(III) is then oxidized to Pu(IV) at the second-step column electrode (E_2 = +0·75 V). The amount of plutonium is determined from the quantity of electricity used at E_2. Uranium does not interfere in the determination of plutonium, as U(VI) is not oxidized at E_2.

Determination of uranium. Uranium in the solution is oxidized to U(VI) and plutonium is reduced to Pu(III) at E_1 = +0·10 V. U(VI) is then reduced to U(IV) at E_2 = −0·60 V. The amount of uranium is determined from the quantity of electricity used at E_2. Plutonium does not interfere with the determination of uranium as Pu(III) is not reduced at E_2.

In this procedure, +0·10 V is used for E_1 but a range from +0·35 to +0·10 V *vs.* SSE is permissible for E_1.

The quantity of electricity used at the second-step column electrode is calculated in terms of weight, and the Pu/(Pu + U) ratio is determined. The results of the determination by this procedure are summarized in Table V.

Determinations are reproducible to within ±3% and blank corrections are not needed for more than 1 μg of plutonium and more than 10 μg of uranium. The sampling by micro-syringe (10 μl) is done with a reproducibility of ±0·1 μl and the current–time curve is integrated with a reproducibility of ±1% for more than 500 mm^2.

CONCLUSION

Two-step flow-coulometry is effective for determination of not only plutonium but also other ionic species which have various oxidation states and are not stable in solution. The method is also applicable to metal ions giving metal as reduction product, *e.g.*, copper. Therefore the method is useful in the differential analysis of mixed samples containing couples with oxidation-reduction potentials close to each other. The size of sample required is small and the method is easily used in remote-control operations. It is expected that successive determination of several elements can be achieved by increasing the number of steps (*i.e.*, columns) used.

Acknowledgement—The authors wish to thank Mr. T. Honda of Japan Atomic Energy Research Institute for his suggestions and the supply of glassy carbon, and Dr. H. Onishi for his helpful advice. The samples of mixed oxides were prepared at the Plutonium Fuel Laboratory in the Japan Atomic Energy Research Institute.

Zusammenfassung—Ein zweistufiges durchflußcoulometrisches Verfahren wurde entwickelt, das zur schnellen Bestimmung von Elementen (Plutonium, Eisen usw.) dient, die in Lösung in verschiedenen Oxidationsstufen vorliegen. Das Verfahren wurde auf die Bestimmung von Plutonium in $0.5M$ Schwefelsäure angewandt. Das Elektrodenpotential in der Säule der ersten Stufe wird zwischen +0·10 und +0·35 V gegen Ag–AgCl festgelegt; hier werden alle Plutoniumionen zu Pu(III) reduziert. Das Elektrodenpotential in der Säule der zweiten Stufe wird bei +0·75 V gegen Ag–AgCl fixiert; hier wird das Pu(III), das von der Elektrode der ersten Säule kommt, zu Pu(IV) oxidiert. Die Plutoniummenge wird aus der bei der Oxidation verbrauchten Anzahl Coulomb bestimmt. Störungen durch verschiedene Ionen können durch Elektroanalyse an der Elektrode der ersten Säule beseitigt werden. Man braucht eine Probe von etwa 10 μl; die Elektrolyse für eine Bestimmung ist in 1 min beendet.

Résumé—On a élaboré une méthode de coulométrie par écoulement à deux temps pour le dosage rapide d'éléments (plutonium, fer, etc.) qui existent à divers stades d'oxydation en solution, et on l'a appliquée au dosage du plutonium en milieu acide sulfurique $0{,}5M$. Le potentiel d'électrode de colonne du premier temps est fixé entre +0,10 et +0,35 V par rapport à Ag–AgCl, et tous les ions plutonium sont réduits à l'état Pu(III). Le potentiel d'électrode de colonne du second temps est fixé à +0,75 V par rapport à Ag–AgCl, et le Pu(III) qui s'écoule de la première électrode de colonne est oxydé en Pu(IV). La quantité de plutonium est déterminée à partir du nombre de coulombs consommés dans l'oxydation. Il est possible d'éliminer l'interférence de divers ions par électroanalyse à la première électrode de colonne. La prise d'essai nécessaire est d'environ 10 μl et l'électroanalyse pour le dosage est terminée en 1 mn.

REFERENCES

1. T. Fujinaga, K. Izutu and S. Okazaki, *Rev. Polarog.* (*Kyoto*), 1967, **14,** 164; T. Fujinaga, *Pure Appl. chem.*, 1971, **25,** 709.
2. G. R. Waterbury and C. F. Metz, *Anal. Chem.*, 1959, **31,** 1144.
3. W. N. Carson, Jr., J. W. Vanderwater and H. S. Gile, *ibid.*, 1957, **29,** 1417.
4. K. Koyama, *ibid.*, 1960, **32,** 523.
5. C. A. Seils, Jr., R. J. Meyer and R. P. Larsen, *ibid.*, 1963, **35,** 1673.
6. S. Kihara, T. Yamamoto, K. Motojima and T. Fujinaga, *Talanta*, 1972, **19,** 329.
7. M. Pages, *J. Chem. Phys.*, 1962, **59,** 63.
8. S. W. Rabideau, *J. Am. Chem. Soc.*, 1957, **79,** 6350.
9. T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1956, **60,** 1956.

Talanta, 1972, Vol. 19, pp. 657 to 668. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF PLUTONIUM BY TWO-STEP FLOW-COULOMETRY AT THE COLUMN ELECTRODE

SORIN KIHARA, TADASHI YAMAMOTO and KENJI MOTOJIMA
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun,
Ibaraki-ken, Japan

and

TAITIRO FUJINAGA
Department of Chemistry, Faculty of Science, Kyoto University,
Kitashirakawa, Sakyo-ku, Kyoto, Japan

(*Received* 12 *November* 1970. *Revised* 25 *April* 1971. *Accepted* 28 *June* 1971)

Summary—A two-step flow-coulometry method has been developed for rapid determination of elements (plutonium, iron, *etc*) which exist in various oxidation states in solution, and applied to the determination of plutonium in 0·5*M* sulphuric acid medium. The first-step column electrode potential is fixed at between +0·10 and +0·35 V *vs.* Ag–AgCl, and all plutonium ions are reduced to Pu(III). The second-step column electrode potential is fixed at +0·75 V *vs.* Ag–AgCl, and Pu(III) which flows from the first column electrode is oxidized to Pu(IV). The quantity of plutonium is determined from the number of coulombs used in the oxidation. It is possible to eliminate interference by diverse ions by electroanalysis at the first column electrode. About a 10-μl sample is necessary and the electrolysis for determination is finished in 1 min.

IT IS WELL KNOWN that plutonium has several oxidation states such as PuO_2^{2+}, PuO_2^{+}, Pu^{4+} and Pu^{3+} in aqueous solution (Pu^{4+} and Pu^{3+} are more stable than the others), and it is difficult to convert them into a single oxidation state by simple chemical procedures. Since plutonium is strongly poisonous, care must be taken in its handling (*e.g.* glove-box operation) and complex procedures are not practical in plutonium analyses.

In this work, the flow-coulometric method[1] has been applied to the determination of plutonium, and a two-step flow-coulometry method has been developed. Micro-amounts of plutonium can be determined precisely by this simple procedure. Plutonium solution (5–50 μl) is passed through the first-step column electrode, which is controlled at a proper potential in order to convert all plutonium into Pu^{3+} ions. The Pu^{3+} ions are passed through the second-step column electrode immediately; here, the working electrode potential is controlled so as to complete the electrode reaction:

$$\mathrm{Pu(III)} - e = \mathrm{Pu(IV)}.$$

The amount of plutonium is then obtained from the integration of the electrolytic current (number of coulombs) at the second-step column electrode:

$$\mathrm{Pu\ (mole)} = \frac{1}{96500}\int_0^\infty i\,\mathrm{d}t$$

where i denotes the oxidation current (A) at time t (sec). The procedure is rapid, and only one minute is required for the whole procedure, including sample injection, valency control at the first-step column electrode and the recording of an electrolytic current at the second-step column electrode. Furthermore, diverse ions which interfere with the determination of plutonium are eliminated at the first-step column electrode by reduction or oxidation.

In the determination of plutonium by electrochemical methods such as potentiometry,[2] coulometry,[3] polarography[4] and amperometry,[5] the oxidation states must be controlled just before the determination. In general, this behaviour of plutonium is a serious source of error in the micro-determination of plutonium. Two-step flow-coulometry, however, will easily be applicable to automatic determination of plutonium in remotely-controlled processes.

EXPERIMENTAL

Reagents

Plutonium. Plutonium metal from Nuclear Materials and Equipment Corporation, U.S.A. (isotopic composition; ^{239}Pu 91·3, ^{240}Pu 7·81, ^{241}Pu 0·85, ^{242}Pu 0·04 atom %) was dissolved in 0·5*M* sulphuric acid after electro-refining and weighing. Plutonium in this solution was expected to be present as a mixture of Pu^{3+}, Pu^{4+} and a small amount of PuO_2^{2+}.

Uranium. Uranium oxide (U_3O_8; Johnson Matthey Co., Ltd.) was dissolved in 6*M* nitric acid and the solution evaporated nearly to dryness. Then the residue was dissolved with small amounts of 0·5*M* sulphuric acid and evaporated almost to dryness. This procedure was repeated three times. The final sulphate solution was prepared by dissolving the residue in 0·5*M* sulphuric acid solution. Uranium in this solution was expected to be present as UO_2^{2+}.

All other reagents used were of extra-pure grade.

Apparatus

The electrolytic cell for two-step flow-coulometry is shown in Fig. 1 and is essentially the same as that described previously[6] except that two column electrodes are used, the distance between them being minimized, and the dispersion of a sample within the carrier solution being kept as small as possible. The glassy carbon counter electrode lasts longer than the silver one used in the previous work.[1] The glassy carbon counter electrodes, however, are not practical in the potential range where electrolysis of the counter electrode solution (saturated potassium chloride solution) takes place markedly. Saturated potassium chloride solution is more suitable for the counter electrode solution than is 0·5*M* sulphuric acid because the solubility of chlorine generated by anodic reaction in saturated potassium chloride solution is greater than that of oxygen generated by anodic reaction in 0·5*M* sulphuric acid.

The glassy carbon working electrode is pretreated as already described. The reference electrode is a saturated KCl–AgCl/Ag electrode (SSE).

Recommended procedure for the determination of plutonium

Pure nitrogen gas is passed through the supporting electrolyte (0·5*M* sulphuric acid) and plutonium sample solution. The supporting electrolyte is passed through the flow-coulometric column electrode at a flow-rate of 5 ± 0·5 ml/min, regulated by varying the height of the solution reservoir. The working potential of the first-column electrode (E_1) is adjusted to +0·35 V *vs.* SSE and that of the second-column electrode (E_2) to +0·75 V *vs.* SSE. Then 10–50 μl of plutonium solution are injected into the supporting electrolyte stream. Plutonium is reduced to Pu(III) at E_1 and Pu(III) is oxidized to Pu(IV) at E_2. The current–time curve for oxidation at E_2 is recorded. The amount of plutonium is determined by integrating the current–time curve and converting the quantity of electricity into weight or concentration.

A blank correction is not needed for the determination of more than 1 μg of plutonium. The total time required for the determination of plutonium (sample injection to recording of current–time curve) is 10–40 sec, depending on the plutonium concentration.

RESULTS AND DISCUSSION

Preliminary studies using the Fe(II)/Fe(III) *couple*

Preliminary studies were made with the Fe(II)/Fe(III) couple as a simple system which has only two oxidation states in aqueous solution. The oxidation-reduction

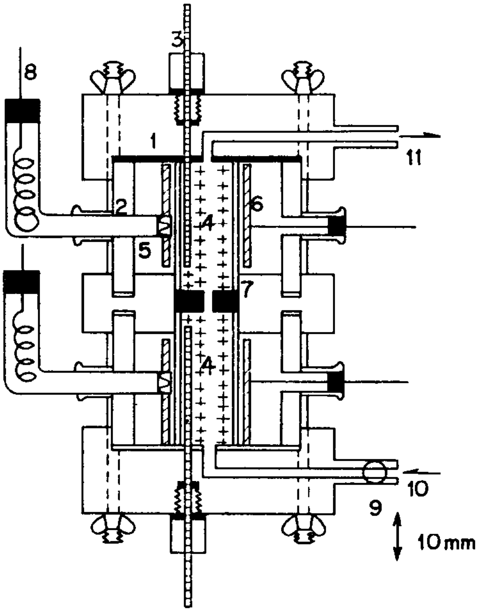


FIG. 1.—Electrolytic cell.
(1) Teflon (2) Glass cylinder
(3) Glassy carbon lead
(4) Glassy carbon grains (working electrode)
(5) Saturated KCl solution
(6) Glassy carbon cylinder (counter electrode)
(7) Porcelain cylinder (8) Ag–AgCl reference electrode
(9) Sample inlet (10) Supporting electrolyte inlet
(11) Supporting electrolyte outlet
■ Silicone rubber.

potential of this couple is near that of the Pu(III)/Pu(IV) couple; the formal oxidation-reduction potentials of Fe(II)/Fe(III) and Pu(III)/Pu(IV) are +0·47 and +0·54 V *vs.* SSE, respectively, in 0·5M sulphuric acid at 25°.

The voltage *vs.* quantity of electricity curves (*E–Q* curves), for the Fe(II)/Fe(III) system in 0·5*M* sulphuric acid, are shown in Fig. 2. Ten μl of 0·02*M* Fe(III) in 0·5*M* sulphuric acid were injected into the carrier solution, *i.e.*, the supporting electrolyte of 0·5*M* sulphuric acid, with the potential at the first-step column electrode (E_1) not applied (open circuit). Curve 1 in Fig. 2 shows the reduction reaction from Fe(III) to Fe(II), on changing the working electrode potential at the second-step column electrode (E_2) from +0·70 to 0·00 V *vs.* SSE.

$$\mathrm{Fe(III)} + e \rightarrow \mathrm{Fe(II)} \quad \text{(Curve 1)}$$

Similarly, curve 2 shows the *E–Q* curve for the oxidation reaction:

$$\mathrm{Fe(II)} - e \rightarrow \mathrm{Fe(III)} \quad \text{(Curve 2)}$$

Curve 3 shows the *E–Q* curve for a mixed sample of 0·0094*M* Fe(III) and 0·0106*M* Fe(II) in 0·5*M* sulphuric acid solution.

From these three curves it is found that if E_1 is +0·10 V *vs.* SSE, Fe(III) ions in the sample solution are all reduced to Fe(II), and the quantity of electricity used in this

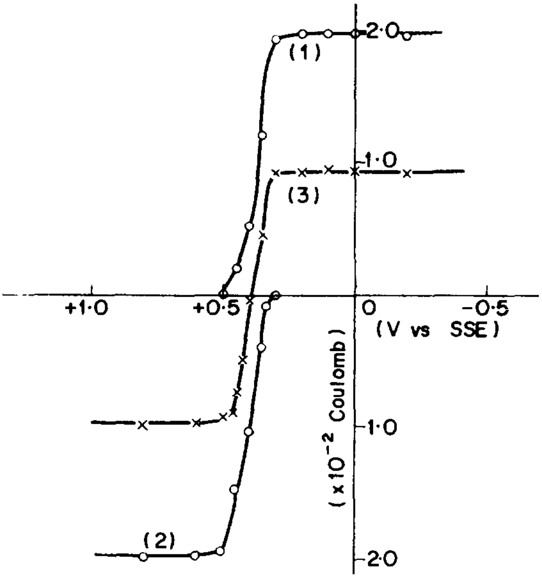


FIG. 2.—Coulomb-potential curves of iron.
Sample: (1) 2 × 10^{-7} mole Fe^{3+}, (2) 2 × 10^{-7} mole Fe^{2+}, (3) 0·94 × 10^{-7} mole Fe^{3+}, 1·06 × 10^{-7} mole Fe^{2+}.
Electrolyte: 0·5*M* H_2SO_4.
Flow-rate: 5 ml/min.

reaction is proportional to the amount of Fe(III) ions in the solution, and if E_1 is controlled to +0·65 V *vs*. SSE, Fe(II) ions in the sample solution are all oxidized to Fe(III), and the quantity of electricity for this reaction is proportional to the amount of Fe(II) ions in the solutions.

With the two column electrodes, E_1 is controlled to +0·10 V *vs*. SSE and E_2 to +0·65 V *vs*. SSE. The quantity of electricity used in the second step shows the total amount of iron in the sample solution. The reaction is then Fe(II) $- e \rightarrow$ Fe(III). Similarly, when E_1 is controlled to +0·65 and E_2 to +0·10 V *vs*. SSE, the electrolytic current at the second-step column electrode shows the total amount of iron at the sample solution but the reaction is Fe(III) $+ e \rightarrow$ Fe(II). Since both of these reactions correspond to one-electron transfers, the absolute values of these two quantities of electricity are 0·0193 C for the 0·200 μ mole of iron taken.

Figures 3*a* and 3*b* show typical coulometry records. The electrolysis begins at the first-step column electrode 3 sec after sample injection, and after 6 sec it occurs at the second-step column electrode (the arrow shows the time of sample injection). About 50 sec are required to complete the electrolysis. Figure 3*a* shows the case where 10 μl of 0·02*M* Fe(III) are reduced at the first-step column electrode (curve 1) and that in which the Fe(II) reduced is oxidized to Fe(III) again at the second-step column electrode (curve 2). The quantities of electricity for these two electrochemical reactions are similar, and are equal to the theoretical value of 0·0193 C. Figure 3*b* shows 10 μl of sample solution, 0·0106*M* Fe(III) and 0·0094*M* Fe(II), reduced at the first-step electrode (E_1 = +0·10 V *vs*. SSE, curve 3) and then oxidized at the second-step electrode (E_2 = +0·65 V *vs*. SSE, curve 5). Curve 4 corresponds to the oxidation of

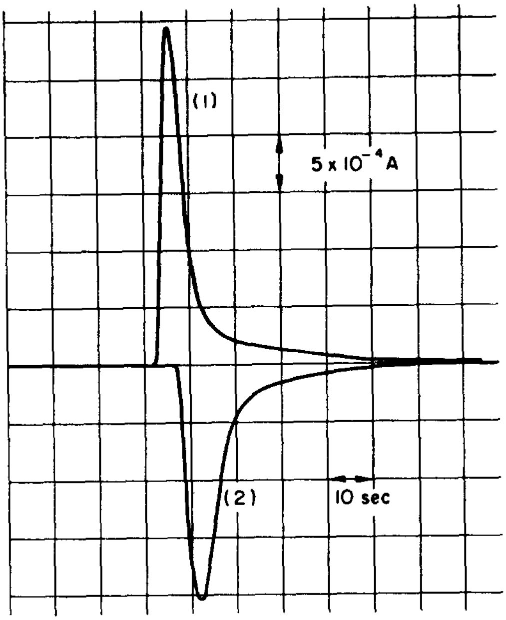


FIG. 3a.—Current-time curve recorded with 10 μl of 2·0 × $10^{-2}M$ Fe(III).
Electrolyte: 0·5M H_2SO_4.
Flow-rate: 5 ml/min.

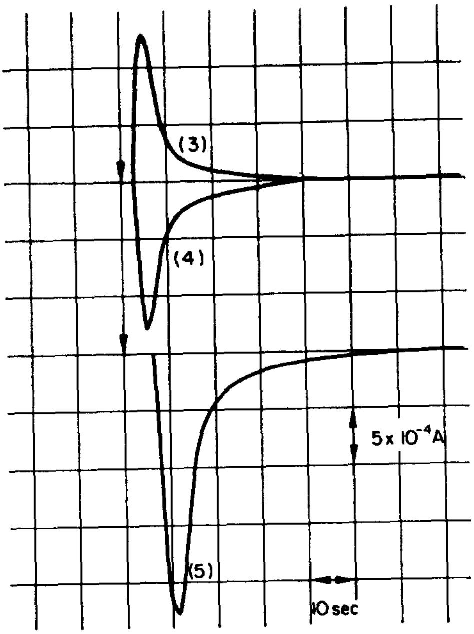


FIG. 3b.—Current-time curve recorded with 10 μl of 1·06 × $10^{-2}M$ Fe(III) + 0·94 × $10^{-2}M$ Fe(II).
Electrolyte: 0·5M H_2SO_4.
Flow-rate: 5 ml/min.

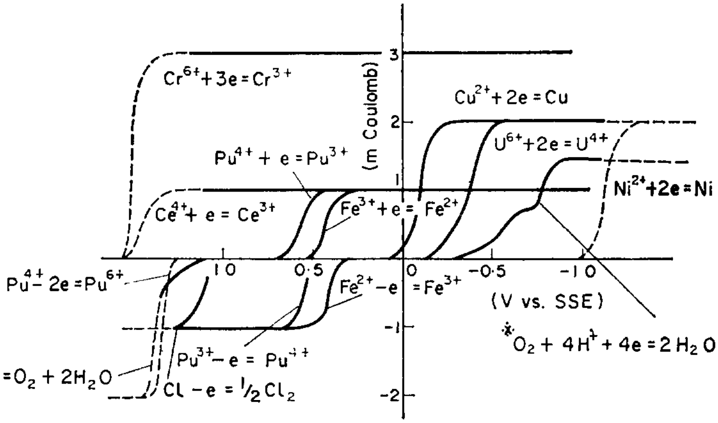


FIG. 4.—Typical coulomb-potential curves of various metal ions at glassy carbon grain column electrode.

Sample: 10^{-8} mole, ·※· 10 μl of air-saturated 0·5M H_2SO_4.

Electrolyte: 0·5M H_2SO_4.

(Broken lines show oxidation or reduction precedes that of samples.)

the solution at the first-step electrode ($E_1 = +0{\cdot}65$ V *vs.* SSE). The sum of the integrated values of curves 3 and 4 is equal to that of curve 5.

E–Q curves of various ions

The *E–Q* curves for the Cu(II)/Cu, U(VI)/U(IV), $\frac{1}{2}Cl_2/Cl^-$, Ce(IV)/Ce(III), Cr(VI)/Cr(III), Ni(II)/Ni, $\frac{1}{2}O_2/H_2O_2$ and $\frac{1}{4}O_2/OH^-$ reactions are shown in Fig. 4. Ten μl of $10^{-3}M$ solutions of various metal ions, chloride ion and hydrogen peroxide and 10 μl of air-saturated 0·5M sulphuric acid, were injected into the carrier solution (0·5M sulphuric acid), with E_1 not applied (open circuit) and *E–Q* curves were obtained by changing E_2. The broken lines show estimated *E–Q* curves because the reduction or oxidation reaction of the elements is preceded by that of the solvent. The oxidation states of iron and plutonium samples were adjusted previously by controlled potential electrolysis.

The *E–Q* curve of Cu(II)/Cu in 0·5M sulphuric acid is about 0·4 V more negative than that of the Fe(III)/Fe(II) couple, as shown in Fig. 4. Therefore copper ions do not interfere with the determinations of iron mentioned above. If E_1 is controlled to $+0{\cdot}65$ V *vs.* SSE and E_2 to $-0{\cdot}25$ V *vs.* SSE, the total amount of iron plus copper ions can be obtained. The difference of these two results (at $E_2 = +0{\cdot}10$ V and $E_2 = -0{\cdot}25$ V) gives the amount of copper ions. The amounts of iron and copper ions could be determined without mutual interference.

Coulometry of plutonium

Figure 4 shows that the cathodic and anodic reactions of the Pu(III)/Pu(IV) couple are both about 0·1 V more positive than those for the Fe(II)/Fe(III) couple. The *E–Q* curves for plutonium are shown in Fig. 5. Ten μl of $4{\cdot}18 \times 10^{-3}M$ plutonium [Pu(III) and Pu(IV) present] solution were used as the sample. Curve 1 shows the reduction reaction of Pu(IV) to Pu(III) on varying E_2 from $+0{\cdot}80$ to $-0{\cdot}20$ V *vs.*

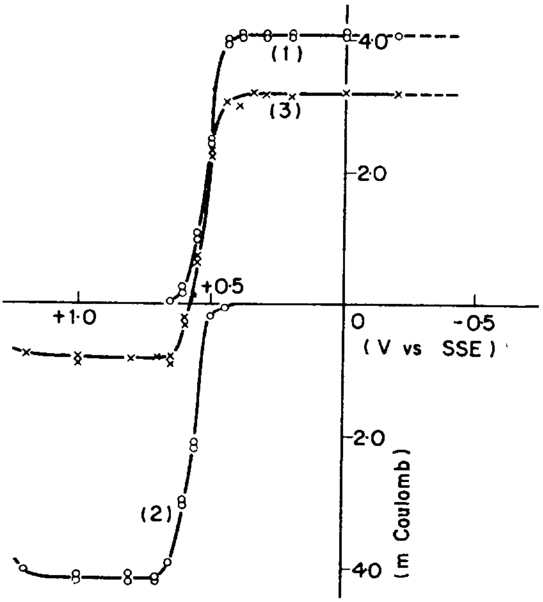


FIG. 5.—Coulomb-potential curves of plutonium.
Sample: 4·18 × 10^{-8} mole Pu.
Electrolyte: 0·5*M* H_2SO_4.
(1) Pu(IV) + *e* = Pu(III).
(2) Pu(III) − *e* = Pu(IV).
(3) Mixture of Pu(III) and Pu(IV).
(The solution was left for five months after dissolution of the plutonium metal.)

SSE. Pu(IV) was produced at the first-step column electrode when potential E_1 was controlled to +0·75 V *vs.* SSE.

$$\text{Pu(IV)} + e \rightarrow \text{Pu(III)} \quad \text{(Curve 1)}$$

Similarly, curve 2 shows the oxidation of Pu(III) to Pu(IV).

$$\text{Pu(III)} - e \rightarrow \text{Pu(IV)} \quad \text{(Curve 2)}$$

Pu(III) was produced at the first-step column electrode, the potential of which was controlled to +0·10 V *vs.* SSE. Curve 3 shows the oxidation and reduction reactions for the mixed solution of Pu(III) and Pu(IV) (a solution which had been left for five months after dissolution of the plutonium metal in 0·5*M* sulphuric acid) when E_1 is not applied (open circuit). It is found from curve 3 that the ratio of Pu(IV) to Pu(III) in this solution is nearly 3:1. In this connection, it is confirmed by comparing curve 3 with curve 2 in Fig. 5, that the presence of Pu(VI) is negligibly small in 0·5*M* sulphuric acid. The sum of the quantity of electricity (Q_3) for reduction at +0·35 V and oxidation at +0·75 V, in curve 3, is nearly equal to the quantity of electricity (Q_2) at +0·75 V in curve 2. If Pu(VI) is present, Q_3 should be larger than Q_2 because, at +0·35 V, Pu(VI) should be reduced to Pu(III) and hence a three-electron change should be involved. After controlled potential electrolysis at +0·75 V at a glassy carbon working electrode, the quantity of electricity used at +0·35 V is nearly equal to Q_2. Therefore, it is considered that the oxidation state of plutonium is Pu(IV) after

TABLE I.—DETERMINATION OF PLUTONIUM

Pu taken	*mmole* taken	Coulombs, calculated	Coulombs, found	Pu found, %
1·03 mg/ml	215	$2·08 \times 10^{-2}$	$2·04 \times 10^{-2}$	98·1
50 μl			2·07	99·5
			2·06	99·0
			2·01	96·7
			2·04	98·1
515 μg/ml	108	$1·04 \times 10^{-2}$	$1·05 \times 10^{-2}$	100·9
50 μl			1·03	99·0
			1·03	99·0
			1·04	99·6
			1·05	100·9
51·5 μg/ml	10·8	$1·04 \times 10^{-3}$	$1·07 \times 10^{-3}$	102·8
50 μl			1·04	99·6
			1·05	100·9
			1·03	98·9
			1·05	100·9
10·3 μg/ml	2·2	$2·08 \times 10^{-4}$	$2·20 \times 10^{-4}$	105·9
50 μl			2·07	99·6
			2·02	97·1
			2·15	103·5
			2·05	98·5
5·0 μg/ml	0·42	$4·02 \times 10^{-5}$	$3·97 \times 10^{-5}$	98·7
20 μl			3·94	98·0
			4·07	101·1
			3·93	97·8
			3·92	97·5

Potentials; first column +0·35 V *vs.* SSE, second column +0·75 V *vs.* SSE.
Electrolyte; 0·5*M* H_2SO_4.
Flow-rate; 5 ml/min.

electrolysis at +0·75 V. The reason why Pu(VI) generated by the disproportionation reaction of Pu(IV) disappears is not clear, but it can be considered that the reduction of Pu(VI) by hydrogen peroxide[7] or α-ray direct reduction[8] and the enhanced complex-forming power of Pu(IV) with sulphate make Pu(VI) unstable. Hydrogen peroxide is generated by radiolysis of water[7] or reduction of dissolved oxygen by Pu(III).[9]

The results of the determination of plutonium by a method based on the information presented in Fig. 5 are summarized in Table I. It is seen that 0·1 μg (0·42 *p* mole) and above of plutonium can be determined within ±3%. This error may be due to an error in sampling and to the current integration procedure.

Elimination of interference by other ions in the determination of plutonium

From Fig. 4, when reducible substances co-exist in a potential range higher than +0·75 V *vs.* SSE, it is seen that plutonium can be determined by the second-step column electrode if $E_1 = +0·75$ and $E_2 = +0·35$ V *vs.* SSE. Similarly, when oxidizable substances co-exist in a potential range lower than +0·35 V *vs.* SSE, plutonium can be determined by the second-step column electrode if $E_1 = +0·35$ and $E_2 = +0·75$ V *vs.* SSE. The results of determination of diverse ions alone, and of plutonium in co-existence with these ions, are summarized in Table II, which shows that plutonium can be determined without interference by these elements.

TABLE II.—EFFECT OF DIVERSE IONS ON DETERMINATION OF PLUTONIUM

Element taken,		Electrode potential (V *vs.* SSE)		Apparent Pu found	
	p mole	first	second	(*p mole*)	%
Ce	642	+0·75	0·00	4·4 3·2 3·2	
Cr	1600	+0·75	0·00	$\sim$0	
Cu	400	+0·75	0·00	2·6 2·0 2·6	
		+0·75	0·00	$\sim$0	
		0·00	+0·75	$\sim$0	
Ni	800	+0·75	0·00	$\sim$0	
		0·00	+0·75	$\sim$0	
U	398	+0·75	0·00	$\sim$0	
		0·00	+0·75	$\sim$0	
Cl	800	+0·75	0·00	$\sim$0	
Pu	41·8	+0·75	+0·10	41·2	101·2
+ Ce	64·2			40·7	99·9
Cr	160			41·9	102·7
Cu	40·1				
Ni	80·0				
U	39·8				
Cl	80·0				

Electrolyte; 0·5M H_2SO_4.
Flow-rate; 5 ml/min.

Coulometric determination of plutonium in the presence of iron

As seen in Fig. 4, the oxidation-reduction potential of the Pu(III)/Pu(IV) couple is similar to that of the Fe(II)/Fe(III) couple, and it is difficult to determine plutonium in the presence of iron by ordinary electrolysis.

The E–Q curves of plutonium (curves 1, 1′) and iron (curves 2, 2′) are shown in Fig. 6. Curves 1 and 2 show the reduction reactions of Pu(IV) and Fe(III), respectively, at $E_1 = +0{\cdot}75$ V *vs.* SSE and varying E_2. Curves 1′ and 2′ show the oxidation reactions of Pu(III) and Fe(II), respectively, at $E_1 = +0{\cdot}10$ V *vs.* SSE and varying E_2. The determination of plutonium in the presence of iron was attempted by varying E_2 with E_1 controlled at +0·75 V *vs.* SSE. The results are shown in Table III. The error in determination is minimum at $E_2 = +0{\cdot}45$ V *vs.* SSE. For $E_2 = +0{\cdot}45$ V and $E_1 = +0{\cdot}75$ V *vs.* SSE, the effect of iron on the determination of plutonium is shown in Table IV. Plutonium in the presence of 6% of its weight of iron can be determined with an error of ±3%.

Differential determination of plutonium and uranium by coulometry

The determination of plutonium and uranium in mixtures is often important, especially when mixed oxides or carbides of plutonium and uranium are used as

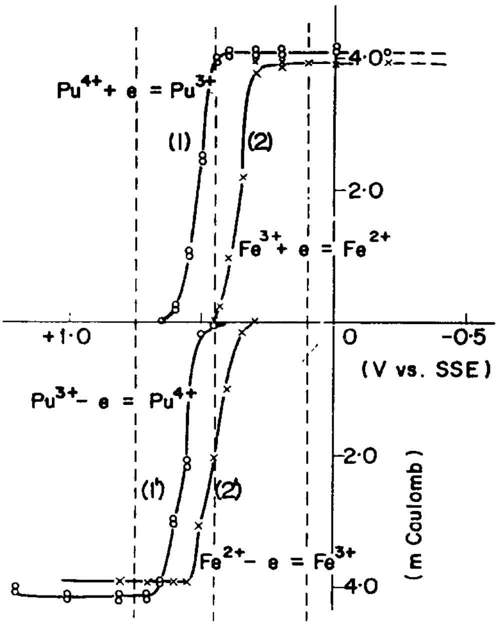


FIG. 6.—Coulomb-potential curves of plutonium and iron.
Sample: Pu 4·18 × 10^{-8} mole, Fe 4·00 × 10^{-8} mole.
Electrolyte: 0·5*M* H_2SO_4.
Flow-rate: 5 ml/min.

TABLE III.—EFFECT OF IRON ON THE DETERMINATION OF PLUTONIUM AT DIFFERENT REDUCTION POTENTIALS

	Second-column potential, *V vs.* SSE			
	+0·500	+0·475	+0·450	+0·425
mC	1·27	1·89	2·20	2·24
found	1·39	1·81	2·21	2·31
	2·41	1·97	2·23	2·30
Theoretical	2·04 mC			

First-column potential; +0·75 V *vs.* SSE.
Electrolyte; 0·5*M* H_2SO_4.
Flow-rate; 5 ml/min.
Sample; 21·1 *p mole* Pu, 20·0 *p mole* Fe.

nuclear fuels. After preliminary studies with plutonium and uranium as described above, a determination procedure for mixed plutonium and uranium oxides has been established. The procedure is as follows.

Determination of the Pu/(Pu + U) *ratio.* The mixed oxide sample (100 mg) is dissolved in 5 ml of 10*M* nitric acid plus 3 drops of 1*M* hydrofluoric acid in 10*M* nitric acid. The nitrate solution is evaporated to near dryness. To the residue are added 10 ml of 0·5*M* sulphuric acid, and the solution is evaporated almost to dryness, and the procedure is repeated three times. The final sample solution is prepared by dissolving the residue in 25 ml of 0·5*M* sulphuric acid, and deaerated by passage of pure nitrogen gas. Ten μl of this solution are taken, and plutonium and uranium determined by two-step flow-coulometry as follows.

Determination of plutonium. Plutonium in the solution is reduced to Pu(III) and uranium is

TABLE IV.—DETERMINATION OF PLUTONIUM IN THE PRESENCE OF IRON

Fe taken, *p mole*	mC found	Pu found (%)
20·0	2·20	107·9
	2·23	109·5
	2·21	108·3
10·0	2·14	104·9
	2·09	102·5
	2·17	106·4
5·00	2·08	102·0
	2·06	101·0
	2·11	103·5

First-column potential; +0·75 V *vs.* SSE.
Second-column potential; +0·45 V *vs.* SSE.
Electrolyte; 0·5M H_2SO_4.
Flow-rate; 5 ml/min.
Sample; 21·1 *p mole* Pu (2·04 mC).

TABLE V.—DETERMINATION OF Pu/(Pu + U) RATIO

Sample nominal ratio, %	Pu found, *mg*	U found, *mg*	Pu/(Pu + U), %
25	21·8	65·5	25·0
	30·4	90·7	25·1
	22·1	66·2	25·1
30	33·3	82·2	28·8
	32·8	84·0	28·1
	32·8	80·1	29·0
33	24·3	49·8	32·8
	23·0	47·0	32·9

oxidized to U(VI) at the first-step column electrode (E_1 = +0·10 V). Pu(III) is then oxidized to Pu(IV) at the second-step column electrode (E_2 = +0·75 V). The amount of plutonium is determined from the quantity of electricity used at E_2. Uranium does not interfere in the determination of plutonium, as U(VI) is not oxidized at E_2.

Determination of uranium. Uranium in the solution is oxidized to U(VI) and plutonium is reduced to Pu(III) at E_1 = +0·10 V. U(VI) is then reduced to U(IV) at E_2 = −0·60 V. The amount of uranium is determined from the quantity of electricity used at E_2. Plutonium does not interfere with the determination of uranium as Pu(III) is not reduced at E_2.

In this procedure, +0·10 V is used for E_1 but a range from +0·35 to +0·10 V *vs.* SSE is permissible for E_1.

The quantity of electricity used at the second-step column electrode is calculated in terms of weight, and the Pu/(Pu + U) ratio is determined. The results of the determination by this procedure are summarized in Table V.

Determinations are reproducible to within ±3% and blank corrections are not needed for more than 1 μg of plutonium and more than 10 μg of uranium. The sampling by micro-syringe (10 μl) is done with a reproducibility of ±0·1 μl and the current-time curve is integrated with a reproducibility of ±1% for more than 500 mm^2.

CONCLUSION

Two-step flow-coulometry is effective for determination of not only plutonium but also other ionic species which have various oxidation states and are not stable in solution. The method is also applicable to metal ions giving metal as reduction product, *e.g.*, copper. Therefore the method is useful in the differential analysis of mixed samples containing couples with oxidation-reduction potentials close to each other. The size of sample required is small and the method is easily used in remote-control operations. It is expected that successive determination of several elements can be achieved by increasing the number of steps (*i.e.*, columns) used.

Acknowledgement—The authors wish to thank Mr. T. Honda of Japan Atomic Energy Research Institute for his suggestions and the supply of glassy carbon, and Dr. H. Onishi for his helpful advice. The samples of mixed oxides were prepared at the Plutonium Fuel Laboratory in the Japan Atomic Energy Research Institute.

Zusammenfassung—Ein zweistufiges durchflußcoulometrisches Verfahren wurde entwickelt, das zur schnellen Bestimmung von Elementen (Plutonium, Eisen usw.) dient, die in Lösung in verschiedenen Oxidationsstufen vorliegen. Das Verfahren wurde auf die Bestimmung von Plutonium in 0.5*M* Schwefelsäure angewandt. Das Elektrodenpotential in der Säule der ersten Stufe wird zwischen +0·10 und +0·35 V gegen Ag–AgCl festgelegt; hier werden alle Plutoniumionen zu Pu(III) reduziert. Das Elektrodenpotential in der Säule der zweiten Stufe wird bei +0·75 V gegen Ag–AgCl fixiert; hier wird das Pu(III), das von der Elektrode der ersten Säule kommt, zu Pu(IV) oxidiert. Die Plutoniummenge wird aus der bei der Oxidation verbrauchten Anzahl Coulomb bestimmt. Störungen durch verschiedene Ionen können durch Elektroanalyse an der Elektrode der ersten Säule beseitigt werden. Man braucht eine Probe von etwa 10 μl; die Elektrolyse für eine Bestimmung ist in 1 min beendet.

Résumé—On a élaboré une méthode de coulométrie par écoulement à deux temps pour le dosage rapide d'éléments (plutonium, fer, etc.) qui existent à divers stades d'oxydation en solution, et on l'a appliquée au dosage du plutonium en milieu acide sulfurique 0,5*M*. Le potentiel d'électrode de colonne du premier temps est fixé entre +0,10 et +0,35 V par rapport à Ag–AgCl, et tous les ions plutonium sont réduits à l'état Pu(III). Le potentiel d'électrode de colonne du second temps est fixé à +0,75 V par rapport à Ag–AgCl, et le Pu(III) qui s'écoule de la première électrode de colonne est oxydé en Pu(IV). La quantité de plutonium est déterminée à partir du nombre de coulombs consommés dans l'oxydation. Il est possible d'éliminer l'interférence de divers ions par électroanalyse à la première électrode de colonne. La prise d'essai nécessaire est d'environ 10 μl et l'électroanalyse pour le dosage est terminée en 1 mn.

REFERENCES

1. T. Fujinaga, K. Izutu and S. Okazaki, *Rev. Polarog.* (*Kyoto*), 1967, **14**, 164; T. Fujinaga, *Pure Appl. chem.*, 1971, **25**, 709.
2. G. R. Waterbury and C. F. Metz, *Anal. Chem.*, 1959, **31**, 1144.
3. W. N. Carson, Jr., J. W. Vanderwater and H. S. Gile, *ibid.*, 1957, **29**, 1417.
4. K. Koyama, *ibid.*, 1960, **32**, 523.
5. C. A. Seils, Jr., R. J. Meyer and R. P. Larsen, *ibid.*, 1963, **35**, 1673.
6. S. Kihara, T. Yamamoto, K. Motojima and T. Fujinaga, *Talanta*, 1972, **19**, 329.
7. M. Pages, *J. Chem. Phys.*, 1962, **59**, 63.
8. S. W. Rabideau, *J. Am. Chem. Soc.*, 1957, **79**, 6350.
9. T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1956, **60**, 1956.

Talanta, 1972, Vol. 19, pp. 669 to 673. Pergamon Press. Printed in Northern Ireland

RAPID ANALYSIS OF FERTILIZERS BY THE DIRECT-READING THERMOMETRIC METHOD

ISTVÁN SAJÓ and B. SIPOS
Research Institute for Ferrous Metallurgy, Budapest, Hungary

(*Received* 4 *December* 1970. *Revised* 10 *September* 1971. *Accepted* 2 *November* 1971)

Summary—The authors have developed rapid methods for the determination of the main components of fertilizers, namely phosphate, potassium and nitrogen fixed in various forms. In the absence of magnesium ions phosphate is precipitated with magnesia mixture; in the presence of magnesium ions ammonium phosphomolybdate is precipitated and the excess of molybdate is reacted with hydrogen peroxide. Potassium is determined by precipitation with silicofluoride. For nitrogen fixed as ammonium salts the ammonium ions are condensed in a basic solution with formalin to hexamethylenetetramine; for nitrogen fixed as carbamide the latter is decomposed with sodium nitrite; for nitrogen fixed as nitrate the latter is reduced with titanium(III). In each case the temperature change of the test solution is measured. Practically all essential components of fertilizers may be determined by direct-reading thermometry; with this method and special apparatus the time of analysis is reduced to at most about 15 min for any determination.

IN DIRECT thermometric analysis a reagent is added to the test solution which reacts selectively with the component in question, and a substantial heat of reaction accompanies the reaction. The temperature variation of the test-solution due to the addition of the reagent is measured, after the reaction is completed. If the reagent is added in excess to the test-solution and the heat-capacity of the system is constant, the temperature variation of the test solution is directly proportional to the concentration of the component in question.[1,2,3] Therefore the concentration of that component can be determined from a single measured value: the temperature change in the sample solution. The results are evaluated either from calibration curves or by direct reading in percentage if the apparatus is built and calibrated for direct-reading thermometric analysis.[4]

The concentration of the dissolved substances may be determined by this method in general within a period of 4–10 min. This method may therefore be used to advantage in the analysis of substances which can be rapidly brought into solution, since if preparation of the test solution is lengthy there cannot be a substantial reduction of the total time of analysis, however rapid the determination itself. In the case of fertilizers the test solutions for the determination of the various components are easily and rapidly prepared and that is why the thermometric method may be used to advantage in the rapid analysis of fertilizers. The test solution does not permit any substantial reduction of the total time of analysis, however rapid the determination itself. In the case of fertilizers the test solutions for the determination of the various components are easily and rapidly prepared and that is why the thermometric method may be used to advantage in the rapid analysis of fertilizers.

EXPERIMENTAL

Equipment and working procedure

In this work we use the same equipment and working procedure described in connection with the analysis of plating baths.[2,4]

Determination of water-soluble P_2O_5 *content*

Principle. Phosphate is precipitated with magnesia mixture as the compound magnesium ammonium phosphate; the temperature change due to the heat of precipitation is measured.

Reagents. Hydrochloric acid, sp. gr. 1·12. Ammonium chloride, solid. Potassium oxalate solution, 30%. Ammonia solution, sp. gr. 0·91. Magnesia mixture. Dissolve 1000 g of $MgCl_2{\cdot}6H_2O$ in 3500 ml of water and add 1000 g of ammonium chloride and 200 ml of ammonia.

Procedure. Pulverize the sample in a porcelain mortar; weigh 10 g of the prepared sample into a 400-ml Stohmann flask, add 400 ml of distilled water and shake vigorously for 30 min on a shaker. Fill up to the mark and mix; filter the solution, discarding the first 20–30 ml of the filtrate, transfer by pipette 100 ml of the filtrate into a 400-ml beaker, add 3 ml of hydrochloric acid, 10 g of ammonium chloride and 5 ml of potassium oxalate solution, neutralize with ammonia, add 5 ml excess of ammonia and dilute to 200 ml with distilled water. Adjust the temperature of this test solution to 1° below the temperature of the measuring cell, place the solution in the measuring cell, add 15 ml of magnesia mixture as reagent and complete the analysis according to the general working procedure. Evaluate the results with the aid of a calibration curve prepared by use of samples of known P_2O_5 content.

If the analysis is carried out in a system without heat of dilution or with compensation of the heat of dilution by a suitable arrangement of the measuring device, the P_2O_5 content can be read directly in percentage on the sensing instrument fitted with a suitable shunt.

The method may be used to determine a water-soluble P_2O_5 content of 3–40% with an error of ±0·3% P_2O_5. One determination takes 10–12 min after preparation of the test solution.

The method may also be used for the determination of the P_2O_5 content of dicalcium phosphate. In this case, however, the sample is dissolved in 100 ml of 0·4*M* hydrochloric acid (for a 1-g sample) and 10 ml of potassium oxalate solution are added to it. The procedure is then the same.

Magnesium in the sample interferes, and in that case an indirect method is used.

Indirect rapid determination of the P_2O_5 *content*

Principle. Phosphate is precipitated with an exactly measured amount of ammonium molybdate solution as ammonium phosphomolybdate; the excess of molybdate is reacted with hydrogen peroxide and the temperature change measured. It is not necessary to filter off the precipitate since the molybdic acid bound in the ammonium phosphomolybdate does not react with hydrogen peroxide.[5]

Reagents. Nitric acid, sp. gr. 1·2. Hydrogen peroxide, 30%. Ammonium molybdate solution. Dissolve 1000 g of ammonium nitrate in 1000 ml of water and heat to 80°. Heat 3000 ml of nitric acid (sp.gr. 1·2) to 80°, pour the ammonium nitrate solution into the nitric acid, and add a solution of 220 g of ammonium molybdate in 1500 ml water which has also been heated previously to 80°. After mixing allow to cool slowly; after two days filter off any precipitate and use the filtrate for analysis.

Procedure. Prepare an aqueous solution of the fertilizer as for the P_2O_5 determination, transfer 10 ml by pipette into a 500-ml beaker, add 40 ml of nitric acid and heat to boiling. To the hot solution add from a burette or pipette an exactly measured 50 ml of molybdate solution. Heat the solution to 80° and stir vigorously at this temperature for 3 min. Cool the solution, transfer it to a 200-ml volumetric flask and dilute to the mark with distilled water. Adjust the initial temperature of the solution to 0·5° below the temperature of the measuring cell, place the solution in the measuring cell, add 5 ml of hydrogen peroxide as reagent and measure the temperature change. Evaluate the results with a calibration curve.

The method may be used to determine a P_2O_5 content of 1–20%; for higher P_2O_5 content the sample weight should be reduced.

The method may be used not only for the determination of the water-soluble P_2O_5 content but also for determining the phosphate content of crude ores used in the production of fertilizers; in this case the phosphate should be brought into solution previously by a treatment with sulphuric or nitric acid.

Determination of the potassium content

It is most convenient to precipitate the potassium as the hexafluorosilicate.[6]

Reagents. Hydrochloric acid, (1 + 1). Hydrofluoric acid, 40%. Precipitating agent. Weigh 100 g of finely powdered silica gel or voluminous precipitated silicic acid into a 2000-ml plastic flask. Slurry with 200 ml of distilled water and add 50 ml of hydrochloric acid (1 + 1). Cool the flask with cold water, add 650 ml of hydrofluoric acid in small portions and leave the mixture until the silica is dissolved.

Procedure. Weigh 20 g of finely powdered fertilizer into a 250-ml volumetric flask, add 200 ml of distilled water and shake the flask vigorously. After 10–15 min, when the potassium salts are dissolved, dilute to volume with distilled water. Mix, filter through a fluted filter, discard the first 10–20 ml of filtrate, transfer 50 ml of filtrate by pipette into a 200-ml polyethylene beaker, add 30 ml of hydrochloric acid and 2 ml of hydrofluoric acid, transfer to a plastic volumetric flask or measuring cylinder and dilute to 200 ml with distilled water. Adjust the initial temperature of the solution to 0·5° below the ambient temperature, place the solution in the measuring cell, add 15 ml of precipitating agent from a platinum or plastic immersion pipette and finish the analysis according to the general working procedure. Evaluate the results with a calibration curve prepared with fertilizers of known potassium oxide content. Direct reading is also possible, as for water-soluble P_2O_5.

The method may be used to determine a K_2O content of 2–40%, on a 20-g sample, with an error of ±0·3% K_2O. One determination takes 20–25 min.

Determination of nitrogen fixed as carbamide

Principle. When carbamide reacts in an acid solution with sodium nitrite it is decomposed with a substantial heat of reaction.

Reagents. Hydrochloric acid, sp.gr. 1·12. Potassium nitrite solution. Saturate a 20% potassium nitrite solution with ammonium sulphate, remove the undissolved ammonium sulphate by filtering and use the filtrate as reagent.

Procedure. Prepare the test solution as described for P_2O_5. Take 50 ml of filtrate by pipette, add 30 ml of hydrochloric acid, filter into a 200-ml volumetric flask and dilute to the mark. Adjust the initial temperature of this test solution to 0·5° below the temperature of the measuring cell. Place the solution in the measuring cell, add 15 ml of potassium nitrite reagent and complete the analysis according to the general working procedure. The reaction does not occur instantaneously, but is completed within about 3 min after addition of the reagent. Evaluate the results with a calibration curve prepared with fertilizer samples of known carbamide content or with model solutions.

A carbamide nitrogen content of 1–20% can be determined in 15 min with an error of ±0·1% N_2. When the nitrite reagent is added to the test solution nitrous gases are formed. Therefore the measuring cell should be placed in a fume cupboard.

Determination of nitrogen fixed as ammonium salts

Principle. Ammonium ions are condensed with formalin in basic solution to hexa-methylenetetramine, with a substantial heat of reaction.

Reagents. Sodium hydroxide solution, 10%. Formalin solution, 20%.

Procedure. Prepare the stock sample solution as before. Transfer 50 ml by pipette into a 200-ml volumetic flask and dilute to the mark with distilled water. Adjust the temperature of this test solution to 0·5° below that of the measuring dell, place the solution in the measuring cell, let the temperature differences equalize, add 10 ml of sodium hydroxide solution, wait for 1 min, then compensate the measuring bridge to adjust the galvanometer pointer to zero. Add 10 ml of formalin solution as reagent and measure the temperature change. Evaluate the results as usual.

The method may be used to determine 1–20% nitrogen fixed as ammonium salts, in 10–15 min, with an error of ±0·2% N_2.

Determination of nitrogen fixed as nitrate

Principle. Nitrate is reduced in acid solution with a mixture of titanium trichloride and stannous chloride and the temperature change is measured.

Reagents. Hydrochloric acid, sp.gr. 1·12. Reducing mixture. Mix 75 ml of 30% titanium trichloride solution with 25 ml of 50% stannous chloride solution.

Procedure. Transfer 50 ml of the stock sample solution by a pipette into a 200-ml volumetric flask, add 10 g of carbamide and 100 ml of hydrochloric acid and dilute to volume with distilled water. Adjust the temperature of this test solution to 0·5° below the temperature of the measuring cell, place the solution in the measuring cell, add 15 ml of the reducing mixture and complete the analysis according to the general working procedure.

A 1–30% nitrate nitrogen content can be determined in 15 min with an error of 0·2% N_2.

RESULTS

Typical results are shown in Tables I and II. The errors quoted above are based on over 100 comparison analyses.

TABLE I.—P_2O_5 AND K_2O CONTENT

Sample	P_2O_5 found, %			K_2O found, %	
	Gravimetric	Direct method	Indirect method	Gravimetric	Thermometric
1	8·40	8·1	8·2	8·15	8·3
2	10·45	10·4	10·1	10·20	10·1
3	12·80	13·0	12·9	12·36	12·1
4	16·80	17·0	17·1	17·96	18·2
5	21·30	21·1	21·0	30·48	30·6
6	10·70	10·8	10·7	10·15	10·2

TABLE II.—NITROGEN CONTENT

Sample	Nitrogen found, %					
	As carbamide		As ammonium salts		As nitrate	
	Volumetric	Thermometric	Volumetric	Thermometric	Volumetric	Thermometric
1			7·69	7·5		
2			9·76	9·9		
3	5·88	5·8	6·15	6·3		
4	6·25	6·2				
6			8·10	8·3	3·22	3·1
7					6·36	6·5
8					6·73	6·9
9	7·16	$7{\cdot}2_5$				
10					8·18	8·0
11	4·75	4·8				
12					4·72	4·5

Zusammenfassung—Die Autoren haben Schnellmethoden zur Bestimmung der Hauptbestandteile von Düngemitteln entwickelt: Phosphat, Kalium und in verschiedenen Formen fixierter Stickstoff. In Abwesenheit von Magnesium wird Phosphat mit Magnesiamixtur gefällt; in Gegenwart von Magnesiumionen wird Ammoniumphosphomolybdat gefällt und das überschüssige Molybdat mit Wasserstoffperoxid zur Reaktion bebracht. Kalium wird durch Fällung mit Silicofluorid bestimmt. Bei in Form von Ammoniumsalzen fixiertem Stickstoff werden die Ammoniumionen in basischem Medium mit Formalin zu Hexamethylentetramin kondensiert; bei als Carbamid fixiertem Stickstoff wird dieses mit Natriumnitrit zersetzt; als Nitrat fixierter Stickstoff wird mit Titan(III) reduziert. In jedem Fall wird die Temperaturänderung der Probelösung gemessen. Praktisch alle wesentlichen Bestandteile von Düngemitteln können durch Thermometrie mit Direktablesung bestimmt werden; mit dieser Methode und einer speziellen Ausrüstung wird die Analysenzeit für eine beliebige Bestimmung auf höchstens etwa 15 min verkürzt.

Résumé—Les auteurs ont élaboré des méthodes rapides pour le dosage des principaux composants d'agents fertilisants, à savoir le phosphate, le potassium et l'azote fixés sous diverses formes. En l'absence d'ions magnésium, on précipite le phosphate par la mixture magnésium; en la présence d'ions magnésium, on précipite le phosphomolybdate d'ammonium et l'on fait régir l'excès de molybdate avec l'eau oxygénée. On dose le potassium par précipitation au fluosilicate.

Pour l'azote fixé à l'état de sels d'ammonium, les ions ammonium sont condensés dans une solution basique avec le formaldéhyde, donnant l'hexaméthylène tétramine; pour l'azote fixé à l'état de carbamide, ce dernier est décomposé par le nitrite de sodium; pour l'azote fixé à l'état de nitrate, ce dernier est réduit par le titane(III). Dans chaque cas, on mesure la variation de température de la solution-essai. Pratiquement, tous les composants essentiels d'agents fertilisants peuvent être déterminés par thermométrie à lecture directe; avec cette méthode et l'appareil spécial, le temps d'analyse est réduit à environ 15 mn au plus pour n'importe quelle détermination.

REFERENCES

1. I. Sajó and J. Ujváry, *Z. Anal. Chem.*, 1964, **202**, 177.
2. I. Sajó and B. Sipos, *ibid.*, 1966, **222**, 23.
3. J. C. Wasilewski, P. T. S. Pey and J. Jordan, *Anal. Chem.*, 1964, **36**, 2131.
4. I. Sajó and B. Sipos, *Talanta*, 1967, **14**, 203.
5. *Idem*, *Mikrochim. Acta*, 1967, **29**, 248.
6. J. Rondeau, M. Legrand and R. A. Paris, *Compt. Rend.* 1966, **263C**, 579.
7. J. Jordan, R. A. Henry and J. C. Wasilewski, *Microchem. J.*, 1966, **10**, 260.

Talanta, 1972, Vol. 19, pp. 669 to 673. Pergamon Press. Printed in Northern Ireland

RAPID ANALYSIS OF FERTILIZERS BY THE DIRECT-READING THERMOMETRIC METHOD

ISTVÁN SAJÓ and B. SIPOS
Research Institute for Ferrous Metallurgy, Budapest, Hungary

(*Received* 4 *December* 1970. *Revised* 10 *September* 1971. *Accepted* 2 *November* 1971)

Summary—The authors have developed rapid methods for the determination of the main components of fertilizers, namely phosphate, potassium and nitrogen fixed in various forms. In the absence of magnesium ions phosphate is precipitated with magnesia mixture; in the presence of magnesium ions ammonium phosphomolybdate is precipitated and the excess of molybdate is reacted with hydrogen peroxide. Potassium is determined by precipitation with silicofluoride. For nitrogen fixed as ammonium salts the ammonium ions are condensed in a basic solution with formalin to hexamethylenetetramine; for nitrogen fixed as carbamide the latter is decomposed with sodium nitrite; for nitrogen fixed as nitrate the latter is reduced with titanium(III). In each case the temperature change of the test solution is measured. Practically all essential components of fertilizers may be determined by direct-reading thermometry; with this method and special apparatus the time of analysis is reduced to at most about 15 min for any determination.

IN DIRECT thermometric analysis a reagent is added to the test solution which reacts selectively with the component in question, and a substantial heat of reaction accompanies the reaction. The temperature variation of the test-solution due to the addition of the reagent is measured, after the reaction is completed. If the reagent is added in excess to the test-solution and the heat-capacity of the system is constant, the temperature variation of the test solution is directly proportional to the concentration of the component in question.[1,2,3] Therefore the concentration of that component can be determined from a single measured value: the temperature change in the sample solution. The results are evaluated either from calibration curves or by direct reading in percentage if the apparatus is built and calibrated for direct-reading thermometric analysis.[4]

The concentration of the dissolved substances may be determined by this method in general within a period of 4–10 min. This method may therefore be used to advantage in the analysis of substances which can be rapidly brought into solution, since if preparation of the test solution is lengthy there cannot be a substantial reduction of the total time of analysis, however rapid the determination itself. In the case of fertilizers the test solutions for the determination of the various components are easily and rapidly prepared and that is why the thermometric method may be used to advantage in the rapid analysis of fertilizers. The test solution does not permit any substantial reduction of the total time of analysis, however rapid the determination itself. In the case of fertilizers the test solutions for the determination of the various components are easily and rapidly prepared and that is why the thermometric method may be used to advantage in the rapid analysis of fertilizers.

EXPERIMENTAL

Equipment and working procedure

In this work we use the same equipment and working procedure described in connection with the analysis of plating baths.[2,4]

Determination of water-soluble P_2O_5 *content*

Principle. Phosphate is precipitated with magnesia mixture as the compound magnesium ammonium phosphate; the temperature change due to the heat of precipitation is measured.

Reagents. Hydrochloric acid, sp. gr. 1·12. Ammonium chloride, solid. Potassium oxalate solution, 30%. Ammonia solution, sp. gr. 0·91. Magnesia mixture. Dissolve 1000 g of $MgCl_2 \cdot 6H_2O$ in 3500 ml of water and add 1000 g of ammonium chloride and 200 ml of ammonia.

Procedure. Pulverize the sample in a porcelain mortar; weigh 10 g of the prepared sample into a 400-ml Stohmann flask, add 400 ml of distilled water and shake vigorously for 30 min on a shaker. Fill up to the mark and mix; filter the solution, discarding the first 20–30 ml of the filtrate, transfer by pipette 100 ml of the filtrate into a 400-ml beaker, add 3 ml of hydrochloric acid, 10 g of ammonium chloride and 5 ml of potassium oxalate solution, neutralize with ammonia, add 5 ml excess of ammonia and dilute to 200 ml with distilled water. Adjust the temperature of this test solution to 1° below the temperature of the measuring cell, place the solution in the measuring cell, add 15 ml of magnesia mixture as reagent and complete the analysis according to the general working procedure. Evaluate the results with the aid of a calibration curve prepared by use of samples of known P_2O_5 content.

If the analysis is carried out in a system without heat of dilution or with compensation of the heat of dilution by a suitable arrangement of the measuring device, the P_2O_5 content can be read directly in percentage on the sensing instrument fitted with a suitable shunt.

The method may be used to determine a water-soluble P_2O_5 content of 3–40% with an error of $\pm 0{\cdot}3\%$ P_2O_5. One determination takes 10–12 min after preparation of the test solution.

The method may also be used for the determination of the P_2O_5 content of dicalcium phosphate. In this case, however, the sample is dissolved in 100 ml of 0·4*M* hydrochloric acid (for a 1-g sample) and 10 ml of potassium oxalate solution are added to it. The procedure is then the same.

Magnesium in the sample interferes, and in that case an indirect method is used.

Indirect rapid determination of the P_2O_5 *content*

Principle. Phosphate is precipitated with an exactly measured amount of ammonium molybdate solution as ammonium phosphomolybdate; the excess of molybdate is reacted with hydrogen peroxide and the temperature change measured. It is not necessary to filter off the precipitate since the molybdic acid bound in the ammonium phosphomolybdate does not react with hydrogen peroxide.[5]

Reagents. Nitric acid, sp. gr. 1·2. Hydrogen peroxide, 30%. Ammonium molybdate solution. Dissolve 1000 g of ammonium nitrate in 1000 ml of water and heat to 80°. Heat 3000 ml of nitric acid (sp.gr. 1·2) to 80°, pour the ammonium nitrate solution into the nitric acid, and add a solution of 220 g of ammonium molybdate in 1500 ml water which has also been heated previously to 80°. After mixing allow to cool slowly; after two days filter off any precipitate and use the filtrate for analysis.

Procedure. Prepare an aqueous solution of the fertilizer as for the P_2O_5 determination, transfer 10 ml by pipette into a 500-ml beaker, add 40 ml of nitric acid and heat to boiling. To the hot solution add from a burette or pipette an exactly measured 50 ml of molybdate solution. Heat the solution to 80° and stir vigorously at this temperature for 3 min. Cool the solution, transfer it to a 200-ml volumetric flask and dilute to the mark with distilled water. Adjust the initial temperature of the solution to 0·5° below the temperature of the measuring cell, place the solution in the measuring cell, add 5 ml of hydrogen peroxide as reagent and measure the temperature change. Evaluate the results with a calibration curve.

The method may be used to determine a P_2O_5 content of 1–20%; for higher P_2O_5 content the sample weight should be reduced.

The method may be used not only for the determination of the water-soluble P_2O_5 content but also for determining the phosphate content of crude ores used in the production of fertilizers; in this case the phosphate should be brought into solution previously by a treatment with sulphuric or nitric acid.

Determination of the potassium content

It is most convenient to precipitate the potassium as the hexafluorosilicate.[6]

Reagents. Hydrochloric acid, (1 + 1). Hydrofluoric acid, 40%. Precipitating agent. Weigh 100 g of finely powdered silica gel or voluminous precipitated silicic acid into a 2000-ml plastic flask. Slurry with 200 ml of distilled water and add 50 ml of hydrochloric acid (1 + 1). Cool the flask with cold water, add 650 ml of hydrofluoric acid in small portions and leave the mixture until the silica is dissolved.

Procedure. Weigh 20 g of finely powdered fertilizer into a 250-ml volumetric flask, add 200 ml of distilled water and shake the flask vigorously. After 10–15 min, when the potassium salts are dissolved, dilute to volume with distilled water. Mix, filter through a fluted filter, discard the first 10–20 ml of filtrate, transfer 50 ml of filtrate by pipette into a 200-ml polyethylene beaker, add 30 ml of hydrochloric acid and 2 ml of hydrofluoric acid, transfer to a plastic volumetric flask or measuring cylinder and dilute to 200 ml with distilled water. Adjust the initial temperature of the solution to 0·5° below the ambient temperature, place the solution in the measuring cell, add 15 ml of precipitating agent from a platinum or plastic immersion pipette and finish the analysis according to the general working procedure. Evaluate the results with a calibration curve prepared with fertilizers of known potassium oxide content. Direct reading is also possible, as for water-soluble P_2O_5.

The method may be used to determine a K_2O content of 2–40%, on a 20-g sample, with an error of ±0·3% K_2O. One determination takes 20–25 min.

Determination of nitrogen fixed as carbamide

Principle. When carbamide reacts in an acid solution with sodium nitrite it is decomposed with a substantial heat of reaction.

Reagents. Hydrochloric acid, sp.gr. 1·12. Potassium nitrite solution. Saturate a 20% potassium nitrite solution with ammonium sulphate, remove the undissolved ammonium sulphate by filtering and use the filtrate as reagent.

Procedure. Prepare the test solution as described for P_2O_5. Take 50 ml of filtrate by pipette, add 30 ml of hydrochloric acid, filter into a 200-ml volumetric flask and dilute to the mark. Adjust the initial temperature of this test solution to 0·5° below the temperature of the measuring cell. Place the solution in the measuring cell, add 15 ml of potassium nitrite reagent and complete the analysis according to the general working procedure. The reaction does not occur instantaneously, but is completed within about 3 min after addition of the reagent. Evaluate the results with a calibration curve prepared with fertilizer samples of known carbamide content or with model solutions.

A carbamide nitrogen content of 1–20% can be determined in 15 min with an error of ±0·1% N_2.

When the nitrite reagent is added to the test solution nitrous gases are formed. Therefore the measuring cell should be placed in a fume cupboard.

Determination of nitrogen fixed as ammonium salts

Principle. Ammonium ions are condensed with formalin in basic solution to hexa-methylenetetramine, with a substantial heat of reaction.

Reagents. Sodium hydroxide solution, 10%. Formalin solution, 20%.

Procedure. Prepare the stock sample solution as before. Transfer 50 ml by pipette into a 200-ml volumetic flask and dilute to the mark with distilled water. Adjust the temperature of this test solution to 0·5° below that of the measuring dell, place the solution in the measuring cell, let the temperature differences equalize, add 10 ml of sodium hydroxide solution, wait for 1 min, then compensate the measuring bridge to adjust the galvanometer pointer to zero. Add 10 ml of formalin solution as reagent and measure the temperature change. Evaluate the results as usual.

The method may be used to determine 1–20% nitrogen fixed as ammonium salts, in 10–15 min, with an error of ±0·2% N_2.

Determination of nitrogen fixed as nitrate

Principle. Nitrate is reduced in acid solution with a mixture of titanium trichloride and stannous chloride and the temperature change is measured.

Reagents. Hydrochloric acid, sp.gr. 1·12. Reducing mixture. Mix 75 ml of 30% titanium trichloride solution with 25 ml of 50% stannous chloride solution.

Procedure. Transfer 50 ml of the stock sample solution by a pipette into a 200-ml volumetric flask, add 10 g of carbamide and 100 ml of hydrochloric acid and dilute to volume with distilled water. Adjust the temperature of this test solution to 0·5° below the temperature of the measuring cell, place the solution in the measuring cell, add 15 ml of the reducing mixture and complete the analysis according to the general working procedure.

A 1–30% nitrate nitrogen content can be determined in 15 min with an error of 0·2% N_2.

RESULTS

Typical results are shown in Tables I and II. The errors quoted above are based on over 100 comparison analyses.

TABLE I.—P_2O_5 AND K_2O CONTENT

Sample	P_2O_5 found, %			K_2O found, %	
	Gravimetric	Direct method	Indirect method	Gravimetric	Thermometric
1	8·40	8·1	8·2	8·15	8·3
2	10·45	10·4	10·1	10·20	10·1
3	12·80	13·0	12·9	12·36	12·1
4	16·80	17·0	17·1	17·96	18·2
5	21·30	21·1	21·0	30·48	30·6
6	10·70	10·8	10·7	10·15	10·2

TABLE II.—NITROGEN CONTENT

Sample	Nitrogen found, %					
	As carbamide		As ammonium salts		As nitrate	
	Volumetric	Thermometric	Volumetric	Thermometric	Volumetric	Thermometric
1			7·69	7·5		
2			9·76	9·9		
3	5·88	5·8	6·15	6·3		
4	6·25	6·2				
6			8·10	8·3	3·22	3·1
7					6·36	6·5
8					6·73	6·9
9	7·16	$7{\cdot}2_5$				
10					8·18	8·0
11	4·75	4·8				
12					4·72	4·5

Zusammenfassung—Die Autoren haben Schnellmethoden zur Bestimmung der Hauptbestandteile von Düngemitteln entwickelt: Phosphat, Kalium und in verschiedenen Formen fixierter Stickstoff. In Abwesenheit von Magnesium wird Phosphat mit Magnesiamixtur gefällt; in Gegenwart von Magnesiumionen wird Ammoniumphosphomolybdat gefällt und das überschüssige Molybdat mit Wasserstoffperoxid zur Reaktion bebracht. Kalium wird durch Fällung mit Silicofluorid bestimmt. Bei in Form von Ammoniumsalzen fixiertem Stickstoff werden die Ammoniumionen in basischem Medium mit Formalin zu Hexamethylentetramin kondensiert; bei als Carbamid fixiertem Stickstoff wird dieses mit Natriumnitrit zersetzt; als Nitrat fixierter Stickstoff wird mit Titan(III) reduziert. In jedem Fall wird die Temperaturänderung der Probelösung gemessen. Praktisch alle wesentlichen Bestandteile von Düngemitteln können durch Thermometrie mit Direktablesung bestimmt werden; mit dieser Methode und einer speziellen Ausrüstung wird die Analysenzeit für eine beliebige Bestimmung auf höchstens etwa 15 min verkürzt.

Résumé—Les auteurs ont élaboré des méthodes rapides pour le dosage des principaux composants d'agents fertilisants, à savoir le phosphate, le potassium et l'azote fixés sous diverses formes. En l'absence d'ions magnésium, on précipite le phosphate par la mixture magnésium; en la présence d'ions magnésium, on précipite le phosphomolybdate d'ammonium et l'on fait régir l'excès de molybdate avec l'eau oxygénée. On dose le potassium par précipitation au fluosilicate.

Pour l'azote fixé à l'état de sels d'ammonium, les ions ammonium sont condensés dans une solution basique avec le formaldéhyde, donnant l'hexaméthylène tétramine; pour l'azote fixé à l'état de carbamide, ce dernier est décomposé par le nitrite de sodium; pour l'azote fixé à l'état de nitrate, ce dernier est réduit par le titane(III). Dans chaque cas, on mesure la variation de température de la solution-essai. Pratiquement, tous les composants essentiels d'agents fertilisants peuvent être déterminés par thermométrie à lecture directe; avec cette méthode et l'appareil spécial, le temps d'analyse est réduit à environ 15 mn au plus pour n'importe quelle détermination.

REFERENCES

1. I. Sajó and J. Ujváry, *Z. Anal. Chem.*, 1964, **202**, 177.
2. I. Sajó and B. Sipos, *ibid.*, 1966, **222**, 23.
3. J. C. Wasilewski, P. T. S. Pey and J. Jordan, *Anal. Chem.*, 1964, **36**, 2131.
4. I. Sajó and B. Sipos, *Talanta*, 1967, **14**, 203.
5. *Idem*, *Mikrochim. Acta*, 1967, **29**, 248.
6. J. Rondeau, M. Legrand and R. A. Paris, *Compt. Rend.* 1966, **263C**, 579.
7. J. Jordan, R. A. Henry and J. C. Wasilewski, *Microchem. J.*, 1966, **10**, 260.

Talanta, 1972, Vol. 19, pp. 675 to 685. Pergamon Press. Printed in Northern Ireland

CATALYTIC REACTIONS—II†

ACTIVATION

P. R. BONTCHEV
Department of Analytical Chemistry, University of Sofia,
1 Anton Ivanov Str., Sofia 26, Bulgaria

(*Received* 19 *May* 1971. *Accepted* 24 *October* 1971)

Summary—The activation of the homogeneous catalytic reactions used in analysis is discussed. The use of activators in catalytic methods permits increase in their sensitivity by 2–4 orders of magnitude and improvement in their selectivity as well. Many different mechanisms of activation are discussed and used as illustrations of the principles for choice of an appropriate activator.

THE MAIN ADVANTAGES that catalytic analysis offers to the analyst are a very high sensitivity and a relative simplicity of the methods used, there being no need for any special apparatus or technique. In many cases, however, the sensitivity of the catalytic methods is too far from maximal and even from the average level in catalytic analysis.

Most catalytic methods of analysis used so far have a sensitivity of the order of 10^{-7}–10^{-9} g/ml. In many cases the sensitivity is even 10^{-10}–10^{-12} g/ml, while for cadmium and lead, for example, it is about 10^{-6} g/ml.

In some other cases, *e.g.*, in reactions catalysed by alkaline earth elements, the catalytic activity shown by the metal ions is very low. This is the reason why catalytic analysis plays a very restricted role in their analytical chemistry and it seems that this situation will remain unchanged unless some new possibilities appear for enhancement of their catalytic activity.

Hence, in spite of the fact that on the whole catalytic analysis has a high average sensitivity, further increase in sensitivity is still a serious and real problem.

The rate of the so-called indicator reaction

$$X + Y \rightarrow P \tag{1}$$

in the presence of the catalyst M^{n+} is given by

$$\text{Rate} = \frac{dP}{dt} = \kappa[X]^p[Y]^q[M^{n+}]^r + k[X]^{p'}[Y]^{q'} \tag{2}$$

where κ is the rate constant of the catalytic reaction ("the catalytic constant"), k is the rate constant of the uncatalysed reaction, and p, q, r, p' and q' are coefficients determined by the reaction equation.

If the reaction scarcely proceeds in the absence of M^{n+}, equation (2) reduces to

$$\text{Rate} = \kappa[X]^p[Y]^q[M^{n+}]^r \tag{3}$$

The possibilities for increase in the reaction sensitivity follow from equations (2) and (3).

The lowest concentration of M^{n+} which can be determined by the use of reaction (1) depends on the lowest amount of the product P that can be estimated for a given

---

† Part I: *Talanta*, 1970, **17**, 499.

interval of time. The sensitivity of the catalytic method is therefore closely related to the method used for monitoring the reaction kinetics. The application of more sensitive methods for determination of the "indicator" substance P increases the sensitivity of the catalytic method.[1]

Thus the determination of S^{2-} based on the iodine-azide reaction was first realized with a sensitivity of the order of $\mu g/ml$, a volumetric technique being used for determination of the reaction product nitrogen.[2] The application of a colorimetric method for monitoring the reaction kinetics increased the sensitivity to 10^{-2} $\mu g/ml$,[3] and by the use of amperometric techniques the determination of sulphide in concentrations as low as 10^{-13} $\mu g/ml$ became possible.[4]

When colorimetric methods are used to follow the reaction kinetics, which is the most frequent case in catalytic analysis, the molar absorptivity of the indicator substance is of prime importance for the sensitivity of the procedure. In this connection the use of quinoidal products or of some dyes as indicator substances might be recommended for highly sensitive catalytic reactions (see Part I).

Another way to increase the catalytic constant and thus the reaction sensitivity, is to carry out the reaction at elevated temperatures. This possibility, however, cannot be used when the uncatalysed reaction also proceeds at a considerable rate at higher temperatures. In such case the rate of the catalytic reaction only is determined as a difference between two large values and the error of the determination becomes too large. There are not many examples of analytical catalytic reactions with low values of the uncatalysed reaction rate and for that reason procedures carried out at temperatures higher than 20–30° are not too common in catalytic analysis.[1]

The possibility that at present seems the most promising for further increase in the catalytic constant and therefore of the sensitivity of catalytic methods is the application of activators.

A review of the literature for the last 6–8 years shows that the most sensitive catalytic methods proposed in this period are connected with the development of the theory and practice of activation of homogeneous catalytic reactions.

By definition, an activator for a homogeneous catalytic reaction is "a substance which does not catalyse this reaction but strongly increases its rate in the presence of certain catalysts."[5]

The mechanism of the activator's action in the process may differ considerably depending on the role of the catalyst in the reaction, the character of the catalyst-activator interaction and the stage of the reaction directly affected by the presence of the activator. Taking into account these factors, activators can be classified into three groups:

(*a*) activators that affect the catalyst–substrate interaction
(*b*) activators that participate in the regeneration of the catalyst
(*c*) activators which act in an indirect way in the catalytic process.

Each will be discussed in turn.

The activator affects the catalyst–substrate interaction

When the catalyst participates in the process through a direct interaction with the substrate (see Part I) the first stage of the catalytic reaction is usually the formation of an intermediate complex M–S.† In this complex further transformations with the substrate take place, having as a final result the formation of the reaction products. In some cases such intermediate complexes have been identified by direct physical methods (EPR, spectral methods), but in many others their formation is assumed on the grounds of kinetic data only (see Part I).

The influence of the activator on this stage of the reaction might affect the formation of the complex M–S and/or its subsequent reactions. In both cases, however, complex formation between the catalyst and the activator is a necessary condition for the activation of the catalytic reaction. In the complex M–A the activator might influence in different ways the reactivity of M towards the reaction substrate.

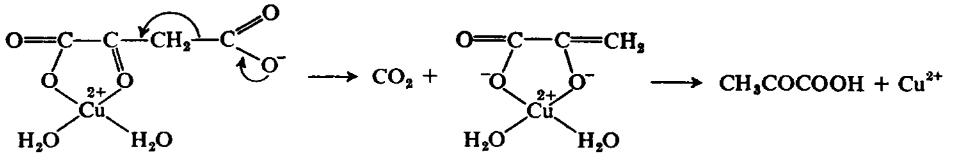
Thus if the activator in M–A can form hydrogen bonds with the substrate it might orient the catalyst and the substrate in a suitable position for the formation of the intermediate M–S. In such cases the activator must possess not only groups capable of keeping together the catalyst and the substrate but also an appropriate structure making possible the interaction of the bound reagents. It is considered, for example, that the activation effect of glycerol in oxidation reactions catalysed by vanadium(V) is of that type.[6] Ethylene glycol shows no effect on the reaction because there is no group in its molecule, co-ordinated to vanadium(V), capable for hydrogen bonding with the substrate, as is the case with the third hydroxyl group of glycerol.

Another example of that type of activation is the catalytic oxidation of aromatic compounds in the presence of Cu(II), activated by hydroxyl ions. According to Yatsimirskii[7] the activation effect is due to the covalent M—OH bond, leading to a more diffuse character of the catalyst's $d_{x^2-y^2}$ orbital and, therefore, to a greater overlap between this orbital and the corresponding filled π-orbitals of the substrate. At the same time the hydroxyl groups in $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ can form hydrogen bonds with the aromatic substrate (usually an arylamine or phenol) and thus also can favour the catalyst–substrate complex formation.

Another reason for the activator's action in this stage of the process might be the increased polarization in the complex M–S when the activator is also included in the co-ordination sphere of the catalyst.

The catalytic activity of metal ions in hydrolytic and decarboxylation reactions is due to the polarization effect of the metal ion on the substrate molecule (see Part I).

For example, the decarboxylation of oxaloacetic acid proceeds in the presence of metal ion catalysts according to the scheme:



(4)

The metal ion catalyst weakens the bond HOOC—CH_2 as a result of the polarization. For this reason the catalytic effect is not a specific one and it might be expected that any increase of the effective charge of the catalyst should result in a higher catalytic activity.

† Here and later in the text M stands for the catalyst, S for the reaction substrate and A for the activator.

We have tried to increase the effective charge on the metal ion in this reaction and, therefore, its catalytic activity, by the use of suitable ligands as activators.[8] Two types of ligands were used for the purpose.

An activator with a lower basicity than the other species in the co-ordination sphere of the catalyst (the substrate and/or the solvent) will cause an increased effective charge on the metal ion. On the other hand, complex formation with such a ligand will take place only if its concentration is much higher than that of the substrate and any other ligands with a higher basicity present in the system.

We were able to demonstrate such an activation on the reaction of catalytic decarboxylation of oxalacetic acid in the presence of Cu^{2+} as a catalyst.[8] The catalytic reaction was carried out in the presence of relatively large amounts of organic oxygen containing solvents, soluble in water, such as ethanol, glycerol, butyric acid and dioxan. In these conditions water is partly displaced by the activator from the co-ordination sphere of Cu^{2+} and ternary complexes of the type catalyst–substrate–activator are formed as intermediates in the course of the catalytic reaction. The existence of copper(II) complexes with the activator in the reaction conditions was confirmed by the use of electronic and EPR spectra.[9]

The other type of ligands used to increase the effective charge of the metal ion catalyst were complexing agents, capable of forming $(M \rightarrow L)$ π-bonds with the catalyst. The formation of such bonds with the activator lowers the electron density on the metal ion catalyst and therefore might be expected to increase its effective charge.

Pyridine, having unoccupied π^* orbitals is a good π-acceptor and it was found[8] that in its presence the rate constant of the model catalytic reaction can be increased by a factor of nearly 8. An analogous effect was found by Rund and Plane[10] with 1,10-phenanthroline and tripyridyl in the decarboxylation of dimethyl oxaloacetate catalysed by Mn^{2+} and Ni^{2+}.

Some steric factors can also be taken into account for a further increase in the activation effect. A good example of this type is the use of 2-methylpyridine as activator in copper(II)-catalysed decarboxylation of oxaloacetic acid.[8] This activator not only increases the effective charge on the metal ion catalyst, but also favours the formation of catalyst–substrate complexes when substrate is being substituted for water and/or the activator in the catalyst co-ordination sphere.

The methyl group in the activator molecule causes steric hindrance in the plane of the square-planar catalyst complexes and thus lowers the energy barrier for the formation of the transition trigonal bipyramidal state. For that reason 2-methylpyridine shows a much higher activation effect than pyridine—it increases the rate constant of the model catalytic reaction by a factor of more than 26.

These investigations served as a basis for the use of decarboxylation reactions in catalytic analysis. Here the catalytic determination of metal ions with a filled outer electron shell must be mentioned first.

The ions of this type usually do not catalyse redox processes and their catalytic activity in hydrolytic and decarboxylation reactions is too low to be of any analytical interest. On the basis of the theoretical considerations above, it was possible to increase the catalytic activity of some of these ions sufficiently and to develop catalytic analytical methods for their determination. Thus in plant materials it was possible to determine catalytically total amounts as low as 5 μg of zinc,[11] 0·5 μg of aluminium,[12] and 50 μg of magnesium.[13]

The activator might also increase the rate of a catalytic reaction through another mechanism—affecting the rate of complex formation between the substrate and the catalyst.

This is, for example, the case with the activating effect of 8-hydroxyquinoline and its derivatives on the oxidation of arylamines by halates, catalysed by vanadium(V).[14] It was shown that in this reaction the activators strongly increase the rate of complex formation between the catalyst and the substrate—the first, rate-limiting step of the overall catalytic reaction. It is supposed that the reason for such action is the *trans*-effect they have on the co-ordination sphere of vanadium(V), in the *xy*-plane.

According to Chatt and Orgel[15] it might be expected that the stronger the electron-acceptor abilities of the ligand, the higher its *trans*-effect and hence its activation action. We have studied this correlation experimentally, varying the substituents in the activator molecule. Thus the presence of two electron-withdrawing groups ($-SO_3H$ and $-I$) in the molecule of 8-hydroxyquinoline strongly increases its electron-acceptor properties and the activation effect connected with them. The rate constant of the model catalytic reaction increases about 36 times when 5-sulpho-7-iodo-8-hydroxyquinoline is substituted for 8-hydroxyquinoline, as activator. The results of these investigations were used for development of a very sensitive method for determination of vanadium in plant materials (sensitivity 10^{-4} μg/ml).[16] Analogous effects were obtained when other electron-acceptors (1,10-phenanthroline, 2,2′-dipyridyl) were used as activators.[17]

Compounds with a system of conjugated π-bonds provide another possibility for activation of redox catalytic reactions. As was shown by Taube[18] such compounds can serve as a bridge between the reagents in electron-transfer reactions. The conjugated system provides a conductive path between the reagents, thus increasing the redox reaction rate. Such substances could be used, therefore, as activators for catalytic reactions where the rate-determining step is electron transfer in the catalyst–substrate interaction. The acceleration of vanadium(V)-catalysed redox reactions by phthalic acid could serve as an illustration of this type of activation.[6]

It must be pointed out that in all cases of activation discussed above, the dependence of the reaction rate on the activator concentration shows a maximum. This is due to the fact that at high activator concentrations the co-ordination sphere of the catalyst is fully occupied by the activator and any complexation with the substrate is prevented.

Nevertheless, in many cases such "blocking" of the co-ordination sphere does not result in a complete quenching of the catalytic activity. If the substitution process

$$MA_n + S \rightleftharpoons MA_{n-1}S + A \qquad (5)$$

proceeds with a measurable rate it will provide a certain concentration of catalyst–substrate complex and therefore some catalytic activity will be obtained. In such conditions the substitution of the activator by the substrate in the co-ordination sphere of the catalyst becomes the rate-limiting step of the overall catalytic reaction.

The existence of a maximum in the curve of reaction rate *vs.* activator concentration is a characteristic feature for all types of activated reactions when the activator action is connected with the formation of ternary complexes of the type A–M–S.

In some cases the activator's influence on the catalytic reaction might be due to a shift in an equilibrium with the participation of the catalyst. This is, for instance, the case with the activation effect of chloride ions on the catalytic decomposition of hydrogen peroxide in the presence of Cu^{2+}.[19]

According to Uri[20] the activation is due to a shift, to the right, of the equilibrium

$$Cu^{2+} + HO_2^- \rightleftharpoons Cu^+ + HO_2^\cdot \tag{6}$$

The overall reaction rate is determined by the position of the equilibrium process, the reactivity of $HO_2^\cdot$ being high enough. Chloride ions, forming more stable complexes with Cu^+ than with Cu^{2+} shift the equilibrium (6) to the right and hence accelerate the catalytic reaction.

A similar fact was found in the catalytic oxidation of arylamines, catalysed by vanadium(V).[21] Recently it was estimated that the highest catalytic activity amongst all ionic species of vanadium(V) is possessed by a form, stable in a very narrow pH-range, which is formed in the process of depolymerization of $H_2V_{10}O_{28}^{4-}$ to VO_2^+.[22] The presence of phosphates, which form complexes with vanadium, shifts the depolymerization equilibrium and thus an activation of the catalytic reaction is observed.[21]

An analogous fact was discovered by Kriss and Yatsimirskii who found that various phosphorus-containing ligands activate the vanadium(V)-catalysed oxidation of iodide by chlorates.[23]

The activator affects the regeneration of the catalyst

Most of the catalysts for homogeneous redox reactions are ions of transition elements that can exist in several oxidation states, *e.g.*, iron, manganese, vanadium, copper, silver. In many reactions of this type the catalyst participates in the process as a mediator for the redox interaction between the reagents, according to the following scheme

$$M^{(n+1)+} + S \rightarrow \text{Products} + M^{n+} \tag{7}$$

$$M^{n+} + Ox \rightarrow M^{(n+1)+} + \text{Red} \tag{8}$$

The catalyst acts by alternate oxidation-reduction steps, any of which can determine the overall reaction rate. Some reactions in which (7) is rate-limiting and which can be affected by activators were discussed in the previous paragraph. Here the cases where (8) determines the overall reaction rate, and therefore could be a means of activation, will be considered.

The theory of Marcus[24] can help to reveal the possibilities for activation of the metal ion–oxidant processes of type (8). According to the theory, for cases when in the transition state a small orbital overlap takes place between the reagents† the rate constant of a redox process is given by the equation

$$k = Z \,.\, \exp\left(-\frac{\Delta G^*}{RT}\right) \tag{9}$$

where Z is the collision number and ΔG^* is the free energy of activation. This last parameter is a function of the standard free energy change of the process, of the charges of the reacting particles, and of terms that account for the solvation of the

---

† It seems that for many cases of direct oxidation of metal ions by oxygen-containing anions this condition is fulfilled.[25]

reagents and the reaction products. Hence, the rate of a catalytic reaction might be increased with activators able to affect these three factors in an appropriate way.[25]

This possibility was demonstrated by the example of silver(I)-catalysed oxidation of sulphanilic acid by peroxydisulphate.[26] The investigations on the reaction mechanism have shown that the process proceeds in two stages, according to (7) and (8), the two oxidation states of the catalyst being Ag(I) and Ag(II) respectively.[27] The rate-determining step of the overall reaction is (8), *i.e.*, the oxidation of Ag(I) to Ag(II).

The application of the Marcus theory to this case has shown that if a neutral ligand capable of complexation with Ag(I) and Ag(II) is added, an acceleration of the process $\mathrm{Ag(I)} - e \rightarrow \mathrm{Ag(II)}$ might be expected. The main contribution to such an effect comes from the lowering of the high oxidation potential of the couple Ag(II)/Ag(I),† *i.e.*, of the free energy change of the process, the role of the other two factors being relatively smaller.

A complexant with nitrogen donors might be expected to cause such a lowering, *i.e.*, to form more stable complexes with Ag^{2+} than with Ag^+ because of the higher charge of Ag^{2+} and of the considerable crystal field stabilization energy (CFSE) for Ag^{2+}, while for Ag^+ CFSE = 0. Polydentate ligands are expected to exhibit a bigger effect, taking into account the difference between the structures of Ag^{2+} and Ag^+ complexes.[28,29]

In complexes with nitrogen-containing ligands Ag(I) has a co-ordination number of 2 and a linear structure of the complexes due to the small difference in energy between the 4*d* and 5*s* orbitals, while a co-ordination number of 4 and a square-planar structure is characteristic for the analogous Ag(II) complexes. The chelate effect can therefore also contribute to a further stabilization of the corresponding Ag(II) complexes. This effect can be still bigger if the polydentate ligand is a strong electron acceptor and can participate in $(M \rightarrow L)$ π-bond formation.

The validity of the theoretical considerations stated above is supported also by the data published in a series of experimental works by Yassinskene and co-workers, who proposed several analytical procedures for determination of silver with the use of nitrogen-containing ligands as activators.[30,31]

The lowering of the oxidation potential can play an important role in reactions where the free-energy change in the reoxidation of the catalyst is high enough to represent the main barrier in the reaction path.

Another mechanism of activation that can affect this stage of the catalytic reaction includes processes where the activator could serve as a matrix for an appropriate orientation of the reagents—the reduced form of the catalyst M^{n+} and the oxidant Ox.

Such a role of the activator could be of importance in cases where several structures of the activated complex $[M^{n+}\text{–}Ox]^*$ could be realized that differ in energy, and the thermodynamically preferred structure is not the most appropriate one for the oxidation process to proceed.[7]

Multidentate activators capable of complexation with M^{n+} and at the same time of forming hydrogen bonds with Ox, could facilitate the formation of the transition state necessary for the oxidation of M^{n+} and thus increase the overall reaction rate. A necessary condition for such an effect is that the structure of the activator must correspond to the inter-atomic distances in the activated complex.

---

† The standard oxidation potential of Ag^{2+}/Ag^+ is $\sim$2·0 V.

Examples of such activators are hydroxycarboxylic acids such as citric, tartaric, for vanadium(V)-catalysed oxidation reactions.[32,33]

Activation of this type is closely connected with the possibility of hydrogen-bonding between the activator and the oxidant. For that reason the activator is very sensitive to any change in its structure that can prevent the formation of such bonds. For example, esterification of the activator's hydroxy groups leads to complete quenching of the activation.[34]

The activator acts in an indirect way in the catalytic process

This group includes activators that participate in parallel processes which can affect the rate of the main catalytic reaction. A typical example of this type of activation is the effect shown by phenols on the catalytic oxidation of some arylamines.[35]

The catalytic oxidation of arylamines proceeds usually by a one-electron mechanism with the formation of free amino-radicals

$$M^{(n+1)+} + ArNH_2 \rightarrow M^{n+} + ArNH^{\cdot} + H^+ \tag{9}$$

which react further to form the final reaction products—quinone-imine compounds (see Part I).

In the presence of phenols an interaction takes place with the primarily formed imino-radicals[36,37]

$$ArOH + ArNH^{\cdot} \rightarrow ArO^{\cdot} + ArNH_2 \tag{10}$$

followed by recombination of $ArO^{\cdot}$ and $ArNH^{\cdot}$ with the formation of quinone-imines:

$$ArO^{\cdot} + ArNH^{\cdot} \rightarrow \text{quinone-imines} \tag{11}$$

Reactions (10) and (11) proceed very rapidly and the rate of quinone-imine formation increases as a result.

In some cases the product of the conjugated oxidation is identical with that of the non-activated reaction and then the term "activation" can be used for the observed increase of the reaction rate. However, as a rule, another quinone-imine compound is obtained in the presence of phenol. Because of the very small differences in the wavelengths of the absorption maxima of similar quinone-imines, the formation of a new reaction product in the presence of such "activators" is very often missed. In spite of the fact that the substrate is used up in the reaction at a higher rate, such cases could scarcely be considered as examples of activation, being in fact only an oxidative coupling.

Thus the oxidation of *p*-phenetidine with chlorate, catalysed by vanadium(V), gives *N*-(4-ethoxyphenyl)quinone-imine as a main oxidation product. The reaction can be activated by the addition of phenol, the product of the oxidative coupling being the same quinone-imine.[38] This activated reaction was used in a sensitive catalytic determination of vanadium.[35]

In the presence of other phenols (such as hydroquinone, catechol, resorcinol, naphthols) the rate of formation of the coloured product strongly increases and the solution seems to keep its red colour unchanged. In fact, chromatographic separation on aluminium oxide, combined with infrared spectral investigations, has shown that different quinone-imines are formed, which absorb in a relatively narrow region of the visible spectrum (500–530 nm).[39]

An analogous mechanism of activation was found[40] for the action of hydroxy- and polycarboxylic acids in arylamine oxidations catalysed by vanadium(V)[40] and chromium(VI).[41] These reactions proceed through a one-electron mechanism, the first, rate-limiting step of the process being the oxidation of the substrate by the catalyst with the formation of arylimino-radicals:

$$S + M^{(n+1)+} \xrightarrow{k_1} S^{\cdot} + M^{n+} \tag{12}$$

The radicals S· then react through recombination or further oxidation to the final reaction products (see Part I).

Hydroxy- and polycarboxylic acids are also oxidized easily by the catalysts to radicals, which then react with the substrate:

$$A + M^{(n+1)+} \xrightarrow{k_2} A^{\cdot} + M^{n+} \tag{13}$$

$$A^{\cdot} + S \xrightarrow{k_3} A \text{ (or } A') + S^{\cdot} \tag{14}$$

An activation effect could be obtained if $k_2 + k_3 > k_1$. Usually the oxidation of polydentate carboxylic acids, such as citric, tartaric, oxalic, proceeds faster than that of the substrates because of the stronger tendency of the catalysts vanadium and chromium for complexation with oxygen than with nitrogen.

The formation of the radicals A· was estimated experimentally.[40] The fact that they really react further with the substrate with the formation of the same reaction products was proved independently.[42] Radicals of type A· were obtained by a photochemical decomposition of trisoxalate iron(III) $Fe(Ox)_3^{3-}$ and their interaction with arylamine substrate studied. It was found that the reaction products thus formed are the same as those obtained when oxalic acid is used as activator.

The investigations on this type of activator served as a basis for development of highly sensitive analytical methods for determination of vanadium and chromium in different materials.[41,43]

In some cases the carboxylic acids used as activators can affect simultaneously several stages of the catalytic reaction through a different mechanism.

Thus the oxidation of *p*-phenetidine with halates, catalysed by vanadium(V), is activated by citric acid. The activator acts in two stages of the reaction: it accelerates the catalyst–substrate interaction through a radical mechanism[40] [according to (13) and (14)] and at the same time increases the rate of regeneration of the catalyst, serving as a matrix for the V(IV)–XO_3^- interaction.[42]

Oxalic acid is also used as an activator for the same reaction, but while a strong effect on the catalyst–substrate interaction is observed,[40] at the same time it acts as an inhibitor for the regeneration of the catalyst.[32] The influence on the first, rate-limiting, stage of the process results in the rates of both reaction stages becoming of the same order and hence the inhibition of the second stage is now of importance. For that reason the total effect of oxalic acid on the overall reaction rate is smaller than that of citric acid.[44]

Another attempt at explanation of the difference in the effect of citric and oxalic acids on the rate-limiting stage and on the overall reaction rate was made by means of molecular orbital theory and the electronic spectra of the catalyst–activator complex.[45] Here the influence of the activator on the second reaction stage was not taken into account at all, the discussion including only the rate-determining step. It was shown that the energy of the charge-transfer band of the complex $M^{(n+1)+}$–A could be used to predict qualitatively the possibility of activation and the order of the activating effect in cases where the activator is oxidized during the reaction, according to (13).

Higher sensitivity is not the only advantage that could be realized by the use of activators in catalytic analysis. Another possibility seems much more attractive—selection of an activator for a given catalytic reaction, that would increase the catalytic activity of the ion to be determined and at the same time quench the activity of other catalysts that can interfere. In such a case an improvement in sensitivity and selectivity could be accomplished simultaneously.

Such a possibility was first pointed out and experimentally realized in 1963 in a catalytic method for determination of vanadium in the presence of copper(II) and iron(III), which also catalyse the indicator reaction.[46] The addition of citric acid increases the sensitivity for vanadium(V) by about 15 times, the activity of both interfering ions being completely suppressed.

The catalytic determination of silver offers another example. Thus 25 μg of silver can be determined catalytically by the sulphanilic acid oxidation, copper(II) and iron(III) interfering in amounts $>0{\cdot}6$ μg and >10 μg respectively.[26] The use of 2,2′-dipyridyl permits the determination of 5×10^{-3} μg of silver (5000 times higher sensitivity) at the same time raising the levels at which copper(II) and iron(III) interfere to 10 and 100 μg respectively.[28] The presence of ethylenediamine increases the sensitivity for silver only 1000 times, but increases tolerance for copper(II) to 50 μg.[29]

It must be pointed out that so far only a few examples of simultaneous improvement of sensitivity and selectivity of catalytic reactions are known. In our opinion, however, this offers one of the most promising lines of research on application of activators in catalytic analysis.

The use of a combination of properly selected activators must also be mentioned as a prospective means of affecting a catalytic reaction. It was shown that sometimes the joint activating effect can be much higher than that of either activator alone.[47] Higher selectivity might also be expected, as shown by Kalinitchenko.[48] This work and other papers by the same author[49–51] are also interesting as examples of the use of activators in catalytic luminescence analysis. The simultaneous application of a system of activators is another promising field for research that could reveal new possibilities for further improvement of catalytic analytical methods.

CONCLUSION

The present paper does not pretend to cover all the data on activators and their application in catalytic analysis. Its aim is only to show the possibilities that the use of activators offers to the analyst, to discuss the mechanisms of their action and on that basis to show the way to select suitable activators for a given catalytic method. This, in our opinion, could help the further development and application of catalytic methods which are amongst the most sensitive modern analytical methods.

Zusammenfassung—Die Aktivierung der analytisch verwendeten homogenen katalytischen Reaktionen wird diskutiert. Die Verwendung von Aktivatoren bei katalytischen Methoden bringt einen Gewinn an Empfindlichkeit von 2–4 Größenordnungen und verbessert außerdem die Selektivität. Viele verschiedene Aktivierungsmechanismen werden diskutiert und als Beispiele für die Gesichtspunkte angeführt, nach denen man einen geeigneten Aktivator auswählt.

Résumé—On discute de l'activation de réactions catalytiques homogènes utilisées en analyse. L'emploi d'activeurs dans les méthodes catalytiques permet d'accroître leur sensibilité d'ordres de grandeur 2–4 et d'améliorer aussi bien leur sélectivité. On discute de nombreux mécanismes différents d'activation et les utilise comme illustration des principes pour le choix d'un activeur approprié.

REFERENCES

1. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, 2nd Ed., Khimia, Moscow, 1967; 1st Ed., Pergamon, Oxford, 1965.
2. T. Shiokawa and S. Suzuki, *J. Chem. Soc. Japan*, 1950, **71**, 629; *Chem. Abstr.*, 1951, **45**, 6538.
3. A. K. Babko and L V. Markova, *Zavodsk. Lab.*, 1959, **25**, 1283.
4. E. Michalski and A. Wtorkowska-Zaremba, *Acta Chim. Soc. Sci. Lodz.*, 1966, **11**, 45.
5. P. R. Bontchev and K. B. Yatsimirskii, *Theoret. Exp. Khim.*, 1965, **1**, 179.
6. P. R. Bontchev, G. Nikolov and B. Lilova, *Ann. Univ. Sofia* (*Khimia*), 1964/65, **59**, 87.
7. K. B. Yatsimirskii, *Kinetics Catalysis* (*USSR*), 1965, **4**, 931.
8. P. R. Bontchev and V. Michaylova, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2945.
9. P. R. Bontchev, N. D. Yordanov and V. Michaylova, *Z. Phys. Chem. Leipzig*, 1969, **242**, 408.
10. J. V. Rund and R. A. Plane, *J. Am. Chem. Soc.*, 1964, **86**, 367.
11. V. Michaylova, B. Evtimova and P. R. Bontchev, *Mikrochim. Acta*, 1968, 922.
12. V. Michaylova and P. R. Bontchev, *ibid.*, 1970, 344.
13. *Idem*, *ibid.*, 1970, 688.
14. P. R. Bontchev and B. G. Jeliazkova, *Inorg. Chim. Acta*, 1967, **1**, 249.
15. J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456; L. E. Orgel, *J. Inorg. Nucl. Chem.*, 1956, **2**, 137.
16. B. G. Jeliazkova, A. L. Tzvetanova and K. B. Yatsimirskii, *Zh. Analit. Khim.*, in the press.
17. P. R. Bontchev and K. Bontcheva, to be published.
18. H. Taube, *Can. J. Chem.*, 1959, **37**, 129.
19. M. Bobtelsky and B. Kirson, *Compt. Rend.*, 1934, **199**, 573.
20. N. Uri, *J. Phys. Colloid. Chem.*, 1949, **53**, 1070.
21. P. R. Bontchev, M. Miteva and B. G. Jeliazkova, *Inorg. Chim. Acta*, 1971, **5**, 75.
22. B. G. Jeliazkova and K. B. Yatsimirskii, *Theoret. Exp. Khim.*, 1972, in the press.
23. E. E. Kriss and K. B. Yatsimirskii, *Zh. Neorgan. Khim.*, 1971, **16**, 386.
24. R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
25. P. R. Bontchev and A. A. Alexiev, *Theoret. Exp. Khim.*, in the press.
26. A. A. Alexiev and P. R. Bontchev, *Mikrochim. Acta*, 1970, 13.
27. P. R. Bontchev and A. A. Alexiev, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2237.
28. P. R. Bontchev, A. A. Alexiev and B. Dimitrova, *Talanta*, 1969, **16**, 597.
29. P. R. Bontchev, A. A. Alexiev and I. Dimitrova, *Mikrochim. Acta*, 1970, 1104.
30. E. Yassinskene and E. Yankauskene, *Zh. Analit. Khim.*, 1966, **21**, 940.
31. E. Yassinskene and N. I. Rasevichute, *ibid.*, 1970, **25**, 458.
32. P. R. Bontchev and Z. Mladenova, *Mikrochim. Acta*, 1967, 427.
33. K. B. Yatsimirskii and V. E. Kalinina, *Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1965, **8**, 385.
34. P. R. Bontchev, *Ukr. Khim. Zh.*, 1964, **30**, 1167.
35. *Idem*, *Mikrochim. Acta*, 1962, 577.
36. S. Hünig and W. Daum, *Annalen*, 1955, **595**, 131.
37. L. K. J. Tong and M. C. Glesmann, *J. Am. Chem. Soc.*, 1968, **90**, 5164.
38. P. R. Bontchev and B. G. Jeliazkova, *Mikrochim. Acta*, 1967, 116.
39. P. R. Bontchev, unpublished results.
40. P. R. Bontchev and K. B. Yatsimirskii, *Zh. Fiz. Khim.*, 1965, **39**, 1995.
41. E. I. Yassinskene and E. B. Bilidene, *Zh. Analit. Khim.*, 1968, **23**, 143.
42. P. R. Bontchev and A. A. Alexiev, *Ukr. Khim. Zh.*, 1966, **32**, 1044.
43. V. M. Zyatkovskii, A. P. Filippov and K. B. Yatsimirskii, in *Methods of Analysis of Chemical Reagents*, 1966, No. 13, p. 69. IREA, Moscow, 1966.
44. P. R. Bontchev and A. A. Alexiev, *Ann. Univ. Sofia* (*Khimia*), 1964/65, **59**, 77.
45. P. R. Bontchev and G. Nikolov, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2609.
46. P. R. Bontchev, *Mikrochim. Acta*, 1964, 79.
47. P. R. Bontchev and B. Evtimova, *ibid.*, 1968, 492.
48. I. E. Kalinitchenko, *Ukr. Khim. Zh.*, 1969, **35**, 755.
49. *Idem*, *ibid.*, 1968, **34**, 307.
50. A. K. Babko and I. E. Kalinitchenko, *ibid.*, 1965, **31**, 948.
51. *Idem*, *ibid.*, 1965, **31**, 1092.

Talanta, 1972, Vol. 19, pp. 675 to 685. Pergamon Press. Printed in Northern Ireland

CATALYTIC REACTIONS—II†

ACTIVATION

P. R. BONTCHEV

Department of Analytical Chemistry, University of Sofia,
1 Anton Ivanov Str., Sofia 26, Bulgaria

(*Received* 19 *May* 1971. *Accepted* 24 *October* 1971)

Summary—The activation of the homogeneous catalytic reactions used in analysis is discussed. The use of activators in catalytic methods permits increase in their sensitivity by 2–4 orders of magnitude and improvement in their selectivity as well. Many different mechanisms of activation are discussed and used as illustrations of the principles for choice of an appropriate activator.

THE MAIN ADVANTAGES that catalytic analysis offers to the analyst are a very high sensitivity and a relative simplicity of the methods used, there being no need for any special apparatus or technique. In many cases, however, the sensitivity of the catalytic methods is too far from maximal and even from the average level in catalytic analysis.

Most catalytic methods of analysis used so far have a sensitivity of the order of 10^{-7}–10^{-9} g/ml. In many cases the sensitivity is even 10^{-10}–10^{-12} g/ml, while for cadmium and lead, for example, it is about 10^{-6} g/ml.

In some other cases, *e.g.*, in reactions catalysed by alkaline earth elements, the catalytic activity shown by the metal ions is very low. This is the reason why catalytic analysis plays a very restricted role in their analytical chemistry and it seems that this situation will remain unchanged unless some new possibilities appear for enhancement of their catalytic activity.

Hence, in spite of the fact that on the whole catalytic analysis has a high average sensitivity, further increase in sensitivity is still a serious and real problem.

The rate of the so-called indicator reaction

$$X + Y \rightarrow P \tag{1}$$

in the presence of the catalyst M^{n+} is given by

$$\text{Rate} = \frac{dP}{dt} = \kappa[X]^p[Y]^q[M^{n+}]^r + k[X]^{p'}[Y]^{q'} \tag{2}$$

where κ is the rate constant of the catalytic reaction ("the catalytic constant"), k is the rate constant of the uncatalysed reaction, and p, q, r, p' and q' are coefficients determined by the reaction equation.

If the reaction scarcely proceeds in the absence of M^{n+}, equation (2) reduces to

$$\text{Rate} = \kappa[X]^p[Y]^q[M^{n+}]^r \tag{3}$$

The possibilities for increase in the reaction sensitivity follow from equations (2) and (3).

The lowest concentration of M^{n+} which can be determined by the use of reaction (1) depends on the lowest amount of the product P that can be estimated for a given

---

† Part I: *Talanta*, 1970, **17**, 499.

interval of time. The sensitivity of the catalytic method is therefore closely related to the method used for monitoring the reaction kinetics. The application of more sensitive methods for determination of the "indicator" substance P increases the sensitivity of the catalytic method.[1]

Thus the determination of S^{2-} based on the iodine-azide reaction was first realized with a sensitivity of the order of μg/ml, a volumetric technique being used for determination of the reaction product nitrogen.[2] The application of a colorimetric method for monitoring the reaction kinetics increased the sensitivity to 10^{-2} μg/ml,[3] and by the use of amperometric techniques the determination of sulphide in concentrations as low as 10^{-13} μg/ml became possible.[4]

When colorimetric methods are used to follow the reaction kinetics, which is the most frequent case in catalytic analysis, the molar absorptivity of the indicator substance is of prime importance for the sensitivity of the procedure. In this connection the use of quinoidal products or of some dyes as indicator substances might be recommended for highly sensitive catalytic reactions (see Part I).

Another way to increase the catalytic constant and thus the reaction sensitivity, is to carry out the reaction at elevated temperatures. This possibility, however, cannot be used when the uncatalysed reaction also proceeds at a considerable rate at higher temperatures. In such case the rate of the catalytic reaction only is determined as a difference between two large values and the error of the determination becomes too large. There are not many examples of analytical catalytic reactions with low values of the uncatalysed reaction rate and for that reason procedures carried out at temperatures higher than 20–30° are not too common in catalytic analysis.[1]

The possibility that at present seems the most promising for further increase in the catalytic constant and therefore of the sensitivity of catalytic methods is the application of activators.

A review of the literature for the last 6–8 years shows that the most sensitive catalytic methods proposed in this period are connected with the development of the theory and practice of activation of homogeneous catalytic reactions.

By definition, an activator for a homogeneous catalytic reaction is "a substance which does not catalyse this reaction but strongly increases its rate in the presence of certain catalysts."[5]

The mechanism of the activator's action in the process may differ considerably depending on the role of the catalyst in the reaction, the character of the catalyst-activator interaction and the stage of the reaction directly affected by the presence of the activator. Taking into account these factors, activators can be classified into three groups:

(*a*) activators that affect the catalyst–substrate interaction
(*b*) activators that participate in the regeneration of the catalyst
(*c*) activators which act in an indirect way in the catalytic process.

Each will be discussed in turn.

The activator affects the catalyst–substrate interaction

When the catalyst participates in the process through a direct interaction with the substrate (see Part I) the first stage of the catalytic reaction is usually the formation of an intermediate complex M–S.† In this complex further transformations with the substrate take place, having as a final result the formation of the reaction products. In some cases such intermediate complexes have been identified by direct physical methods (EPR, spectral methods), but in many others their formation is assumed on the grounds of kinetic data only (see Part I).

The influence of the activator on this stage of the reaction might affect the formation of the complex M–S and/or its subsequent reactions. In both cases, however, complex formation between the catalyst and the activator is a necessary condition for the activation of the catalytic reaction. In the complex M–A the activator might influence in different ways the reactivity of M towards the reaction substrate.

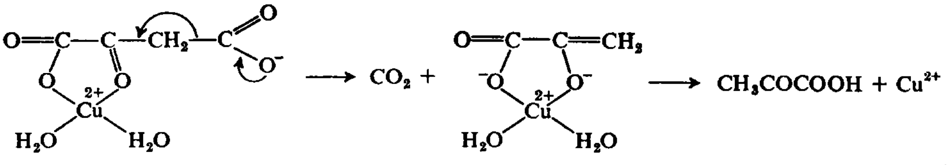
Thus if the activator in M–A can form hydrogen bonds with the substrate it might orient the catalyst and the substrate in a suitable position for the formation of the intermediate M–S. In such cases the activator must possess not only groups capable of keeping together the catalyst and the substrate but also an appropriate structure making possible the interaction of the bound reagents. It is considered, for example, that the activation effect of glycerol in oxidation reactions catalysed by vanadium(V) is of that type.[6] Ethylene glycol shows no effect on the reaction because there is no group in its molecule, co-ordinated to vanadium(V), capable for hydrogen bonding with the substrate, as is the case with the third hydroxyl group of glycerol.

Another example of that type of activation is the catalytic oxidation of aromatic compounds in the presence of Cu(II), activated by hydroxyl ions. According to Yatsimirskii[7] the activation effect is due to the covalent M—OH bond, leading to a more diffuse character of the catalyst's $d_{x^2-y^2}$ orbital and, therefore, to a greater overlap between this orbital and the corresponding filled π-orbitals of the substrate. At the same time the hydroxyl groups in $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ can form hydrogen bonds with the aromatic substrate (usually an arylamine or phenol) and thus also can favour the catalyst–substrate complex formation.

Another reason for the activator's action in this stage of the process might be the increased polarization in the complex M–S when the activator is also included in the co-ordination sphere of the catalyst.

The catalytic activity of metal ions in hydrolytic and decarboxylation reactions is due to the polarization effect of the metal ion on the substrate molecule (see Part I).

For example, the decarboxylation of oxaloacetic acid proceeds in the presence of metal ion catalysts according to the scheme:



(4)

The metal ion catalyst weakens the bond HOOC—CH_2 as a result of the polarization. For this reason the catalytic effect is not a specific one and it might be expected that any increase of the effective charge of the catalyst should result in a higher catalytic activity.

---

† Here and later in the text M stands for the catalyst, S for the reaction substrate and A for the activator.

We have tried to increase the effective charge on the metal ion in this reaction and, therefore, its catalytic activity, by the use of suitable ligands as activators.[8] Two types of ligands were used for the purpose.

An activator with a lower basicity than the other species in the co-ordination sphere of the catalyst (the substrate and/or the solvent) will cause an increased effective charge on the metal ion. On the other hand, complex formation with such a ligand will take place only if its concentration is much higher than that of the substrate and any other ligands with a higher basicity present in the system.

We were able to demonstrate such an activation on the reaction of catalytic decarboxylation of oxalacetic acid in the presence of Cu^{2+} as a catalyst.[8] The catalytic reaction was carried out in the presence of relatively large amounts of organic oxygen containing solvents, soluble in water, such as ethanol, glycerol, butyric acid and dioxan. In these conditions water is partly displaced by the activator from the co-ordination sphere of Cu^{2+} and ternary complexes of the type catalyst–substrate–activator are formed as intermediates in the course of the catalytic reaction. The existence of copper(II) complexes with the activator in the reaction conditions was confirmed by the use of electronic and EPR spectra.[9]

The other type of ligands used to increase the effective charge of the metal ion catalyst were complexing agents, capable of forming $(M \rightarrow L)$ π-bonds with the catalyst. The formation of such bonds with the activator lowers the electron density on the metal ion catalyst and therefore might be expected to increase its effective charge.

Pyridine, having unoccupied π^* orbitals is a good π-acceptor and it was found[8] that in its presence the rate constant of the model catalytic reaction can be increased by a factor of nearly 8. An analogous effect was found by Rund and Plane[10] with 1,10-phenanthroline and tripyridyl in the decarboxylation of dimethyl oxaloacetate catalysed by Mn^{2+} and Ni^{2+}.

Some steric factors can also be taken into account for a further increase in the activation effect. A good example of this type is the use of 2-methylpyridine as activator in copper(II)-catalysed decarboxylation of oxaloacetic acid.[8] This activator not only increases the effective charge on the metal ion catalyst, but also favours the formation of catalyst–substrate complexes when substrate is being substituted for water and/or the activator in the catalyst co-ordination sphere.

The methyl group in the activator molecule causes steric hindrance in the plane of the square-planar catalyst complexes and thus lowers the energy barrier for the formation of the transition trigonal bipyramidal state. For that reason 2-methylpyridine shows a much higher activation effect than pyridine—it increases the rate constant of the model catalytic reaction by a factor of more than 26.

These investigations served as a basis for the use of decarboxylation reactions in catalytic analysis. Here the catalytic determination of metal ions with a filled outer electron shell must be mentioned first.

The ions of this type usually do not catalyse redox processes and their catalytic activity in hydrolytic and decarboxylation reactions is too low to be of any analytical interest. On the basis of the theoretical considerations above, it was possible to increase the catalytic activity of some of these ions sufficiently and to develop catalytic analytical methods for their determination. Thus in plant materials it was possible to determine catalytically total amounts as low as 5 μg of zinc,[11] 0·5 μg of aluminium,[12] and 50 μg of magnesium.[13]

The activator might also increase the rate of a catalytic reaction through another mechanism—affecting the rate of complex formation between the substrate and the catalyst.

This is, for example, the case with the activating effect of 8-hydroxyquinoline and its derivatives on the oxidation of arylamines by halates, catalysed by vanadium(V).[14] It was shown that in this reaction the activators strongly increase the rate of complex formation between the catalyst and the substrate—the first, rate-limiting step of the overall catalytic reaction. It is supposed that the reason for such action is the *trans*-effect they have on the co-ordination sphere of vanadium(V), in the xy-plane.

According to Chatt and Orgel[15] it might be expected that the stronger the electron-acceptor abilities of the ligand, the higher its *trans*-effect and hence its activation action. We have studied this correlation experimentally, varying the substituents in the activator molecule. Thus the presence of two electron-withdrawing groups ($-SO_3H$ and $-I$) in the molecule of 8-hydroxyquinoline strongly increases its electron-acceptor properties and the activation effect connected with them. The rate constant of the model catalytic reaction increases about 36 times when 5-sulpho-7-iodo-8-hydroxyquinoline is substituted for 8-hydroxyquinoline, as activator. The results of these investigations were used for development of a very sensitive method for determination of vanadium in plant materials (sensitivity 10^{-4} μg/ml).[16] Analogous effects were obtained when other electron-acceptors (1,10-phenanthroline, 2,2′-dipyridyl) were used as activators.[17]

Compounds with a system of conjugated π-bonds provide another possibility for activation of redox catalytic reactions. As was shown by Taube[18] such compounds can serve as a bridge between the reagents in electron-transfer reactions. The conjugated system provides a conductive path between the reagents, thus increasing the redox reaction rate. Such substances could be used, therefore, as activators for catalytic reactions where the rate-determining step is electron transfer in the catalyst–substrate interaction. The acceleration of vanadium(V)-catalysed redox reactions by phthalic acid could serve as an illustration of this type of activation.[6]

It must be pointed out that in all cases of activation discussed above, the dependence of the reaction rate on the activator concentration shows a maximum. This is due to the fact that at high activator concentrations the co-ordination sphere of the catalyst is fully occupied by the activator and any complexation with the substrate is prevented.

Nevertheless, in many cases such "blocking" of the co-ordination sphere does not result in a complete quenching of the catalytic activity. If the substitution process

$$MA_n + S \rightleftharpoons MA_{n-1}S + A \tag{5}$$

proceeds with a measurable rate it will provide a certain concentration of catalyst–substrate complex and therefore some catalytic activity will be obtained. In such conditions the substitution of the activator by the substrate in the co-ordination sphere of the catalyst becomes the rate-limiting step of the overall catalytic reaction.

The existence of a maximum in the curve of reaction rate *vs.* activator concentration is a characteristic feature for all types of activated reactions when the activator action is connected with the formation of ternary complexes of the type A–M–S.

In some cases the activator's influence on the catalytic reaction might be due to a shift in an equilibrium with the participation of the catalyst. This is, for instance, the case with the activation effect of chloride ions on the catalytic decomposition of hydrogen peroxide in the presence of Cu^{2+}.[19]

According to Uri[20] the activation is due to a shift, to the right, of the equilibrium

$$Cu^{2+} + HO_2^- \rightleftharpoons Cu^+ + HO_2^\cdot \qquad (6)$$

The overall reaction rate is determined by the position of the equilibrium process, the reactivity of $HO_2^\cdot$ being high enough. Chloride ions, forming more stable complexes with Cu^+ than with Cu^{2+} shift the equilibrium (6) to the right and hence accelerate the catalytic reaction.

A similar fact was found in the catalytic oxidation of arylamines, catalysed by vanadium(V).[21] Recently it was estimated that the highest catalytic activity amongst all ionic species of vanadium(V) is possessed by a form, stable in a very narrow pH-range, which is formed in the process of depolymerization of $H_2V_{10}O_{28}^{4-}$ to VO_2^+.[22] The presence of phosphates, which form complexes with vanadium, shifts the depolymerization equilibrium and thus an activation of the catalytic reaction is observed.[21]

An analogous fact was discovered by Kriss and Yatsimirskii who found that various phosphorus-containing ligands activate the vanadium(V)-catalysed oxidation of iodide by chlorates.[23]

The activator affects the regeneration of the catalyst

Most of the catalysts for homogeneous redox reactions are ions of transition elements that can exist in several oxidation states, *e.g.*, iron, manganese, vanadium, copper, silver. In many reactions of this type the catalyst participates in the process as a mediator for the redox interaction between the reagents, according to the following scheme

$$M^{(n+1)+} + S \rightarrow \text{Products} + M^{n+} \qquad (7)$$

$$M^{n+} + Ox \rightarrow M^{(n+1)+} + \text{Red} \qquad (8)$$

The catalyst acts by alternate oxidation-reduction steps, any of which can determine the overall reaction rate. Some reactions in which (7) is rate-limiting and which can be affected by activators were discussed in the previous paragraph. Here the cases where (8) determines the overall reaction rate, and therefore could be a means of activation, will be considered.

The theory of Marcus[24] can help to reveal the possibilities for activation of the metal ion–oxidant processes of type (8). According to the theory, for cases when in the transition state a small orbital overlap takes place between the reagents† the rate constant of a redox process is given by the equation

$$k = Z \,.\, \exp\left(-\frac{\Delta G^*}{RT}\right) \qquad (9)$$

where Z is the collision number and ΔG^* is the free energy of activation. This last parameter is a function of the standard free energy change of the process, of the charges of the reacting particles, and of terms that account for the solvation of the

---

† It seems that for many cases of direct oxidation of metal ions by oxygen-containing anions this condition is fulfilled.[25]

reagents and the reaction products. Hence, the rate of a catalytic reaction might be increased with activators able to affect these three factors in an appropriate way.[25]

This possibility was demonstrated by the example of silver(I)-catalysed oxidation of sulphanilic acid by peroxydisulphate.[26] The investigations on the reaction mechanism have shown that the process proceeds in two stages, according to (7) and (8), the two oxidation states of the catalyst being Ag(I) and Ag(II) respectively.[27] The rate-determining step of the overall reaction is (8), *i.e.*, the oxidation of Ag(I) to Ag(II).

The application of the Marcus theory to this case has shown that if a neutral ligand capable of complexation with Ag(I) and Ag(II) is added, an acceleration of the process Ag(I) $-$ *e* → Ag(II) might be expected. The main contribution to such an effect comes from the lowering of the high oxidation potential of the couple Ag(II)/Ag(I),† *i.e.*, of the free energy change of the process, the role of the other two factors being relatively smaller.

A complexant with nitrogen donors might be expected to cause such a lowering, *i.e.*, to form more stable complexes with Ag^{2+} than with Ag^+ because of the higher charge of Ag^{2+} and of the considerable crystal field stabilization energy (CFSE) for Ag^{2+}, while for Ag^+ CFSE = 0. Polydentate ligands are expected to exhibit a bigger effect, taking into account the difference between the structures of Ag^{2+} and Ag^+ complexes.[28,29]

In complexes with nitrogen-containing ligands Ag(I) has a co-ordination number of 2 and a linear structure of the complexes due to the small difference in energy between the 4*d* and 5*s* orbitals, while a co-ordination number of 4 and a square-planar structure is characteristic for the analogous Ag(II) complexes. The chelate effect can therefore also contribute to a further stabilization of the corresponding Ag(II) complexes. This effect can be still bigger if the polydentate ligand is a strong electron acceptor and can participate in (M → L) π-bond formation.

The validity of the theoretical considerations stated above is supported also by the data published in a series of experimental works by Yassinskene and co-workers, who proposed several analytical procedures for determination of silver with the use of nitrogen-containing ligands as activators.[30,31]

The lowering of the oxidation potential can play an important role in reactions where the free-energy change in the reoxidation of the catalyst is high enough to represent the main barrier in the reaction path.

Another mechanism of activation that can affect this stage of the catalytic reaction includes processes where the activator could serve as a matrix for an appropriate orientation of the reagents—the reduced form of the catalyst M^{n+} and the oxidant Ox.

Such a role of the activator could be of importance in cases where several structures of the activated complex $[M^{n+}\text{–}Ox]^*$ could be realized that differ in energy, and the thermodynamically preferred structure is not the most appropriate one for the oxidation process to proceed.[7]

Multidentate activators capable of complexation with M^{n+} and at the same time of forming hydrogen bonds with Ox, could facilitate the formation of the transition state necessary for the oxidation of M^{n+} and thus increase the overall reaction rate. A necessary condition for such an effect is that the structure of the activator must correspond to the inter-atomic distances in the activated complex.

† The standard oxidation potential of Ag^{2+}/Ag^+ is ~2·0 V.

Examples of such activators are hydroxycarboxylic acids such as citric, tartaric, for vanadium(V)-catalysed oxidation reactions.[32,33]

Activation of this type is closely connected with the possibility of hydrogen-bonding between the activator and the oxidant. For that reason the activator is very sensitive to any change in its structure that can prevent the formation of such bonds. For example, esterification of the activator's hydroxy groups leads to complete quenching of the activation.[34]

The activator acts in an indirect way in the catalytic process

This group includes activators that participate in parallel processes which can affect the rate of the main catalytic reaction. A typical example of this type of activation is the effect shown by phenols on the catalytic oxidation of some arylamines.[35]

The catalytic oxidation of arylamines proceeds usually by a one-electron mechanism with the formation of free amino-radicals

$$M^{(n+1)+} + ArNH_2 \rightarrow M^{n+} + ArNH^{\cdot} + H^+ \qquad (9)$$

which react further to form the final reaction products—quinone-imine compounds (see Part I).

In the presence of phenols an interaction takes place with the primarily formed imino-radicals[36,37]

$$ArOH + ArNH^{\cdot} \rightarrow ArO^{\cdot} + ArNH_2 \qquad (10)$$

followed by recombination of $ArO^{\cdot}$ and $ArNH^{\cdot}$ with the formation of quinone-imines:

$$ArO^{\cdot} + ArNH^{\cdot} \rightarrow \text{quinone-imines} \qquad (11)$$

Reactions (10) and (11) proceed very rapidly and the rate of quinone-imine formation increases as a result.

In some cases the product of the conjugated oxidation is identical with that of the non-activated reaction and then the term "activation" can be used for the observed increase of the reaction rate. However, as a rule, another quinone-imine compound is obtained in the presence of phenol. Because of the very small differences in the wavelengths of the absorption maxima of similar quinone-imines, the formation of a new reaction product in the presence of such "activators" is very often missed. In spite of the fact that the substrate is used up in the reaction at a higher rate, such cases could scarcely be considered as examples of activation, being in fact only an oxidative coupling.

Thus the oxidation of *p*-phenetidine with chlorate, catalysed by vanadium(V), gives *N*-(4-ethoxyphenyl)quinone-imine as a main oxidation product. The reaction can be activated by the addition of phenol, the product of the oxidative coupling being the same quinone-imine.[38] This activated reaction was used in a sensitive catalytic determination of vanadium.[35]

In the presence of other phenols (such as hydroquinone, catechol, resorcinol, naphthols) the rate of formation of the coloured product strongly increases and the solution seems to keep its red colour unchanged. In fact, chromatographic separation on aluminium oxide, combined with infrared spectral investigations, has shown that different quinone-imines are formed, which absorb in a relatively narrow region of the visible spectrum (500–530 nm).[39]

An analogous mechanism of activation was found[40] for the action of hydroxy- and polycarboxylic acids in arylamine oxidations catalysed by vanadium(V)[40] and chromium(VI).[41] These reactions proceed through a one-electron mechanism, the first, rate-limiting step of the process being the oxidation of the substrate by the catalyst with the formation of arylimino-radicals:

$$\mathrm{S} + \mathrm{M}^{(n+1)+} \xrightarrow{k_1} \mathrm{S}^{\cdot} + \mathrm{M}^{n+} \qquad (12)$$

The radicals $\mathrm{S}^{\cdot}$ then react through recombination or further oxidation to the final reaction products (see Part I).

Hydroxy- and polycarboxylic acids are also oxidized easily by the catalysts to radicals, which then react with the substrate:

$$\mathrm{A} + \mathrm{M}^{(n+1)+} \xrightarrow{k_2} \mathrm{A}^{\cdot} + \mathrm{M}^{n+} \qquad (13)$$

$$\mathrm{A}^{\cdot} + \mathrm{S} \xrightarrow{k_3} \mathrm{A}\ (\text{or } \mathrm{A}') + \mathrm{S}^{\cdot} \qquad (14)$$

An activation effect could be obtained if $k_2 + k_3 > k_1$. Usually the oxidation of polydentate carboxylic acids, such as citric, tartaric, oxalic, proceeds faster than that of the substrates because of the stronger tendency of the catalysts vanadium and chromium for complexation with oxygen than with nitrogen.

The formation of the radicals $\mathrm{A}^{\cdot}$ was estimated experimentally.[40] The fact that they really react further with the substrate with the formation of the same reaction products was proved independently.[42] Radicals of type $\mathrm{A}^{\cdot}$ were obtained by a photochemical decomposition of trisoxalate iron(III) $\mathrm{Fe(Ox)_3^{3-}}$ and their interaction with arylamine substrate studied. It was found that the reaction products thus formed are the same as those obtained when oxalic acid is used as activator.

The investigations on this type of activator served as a basis for development of highly sensitive analytical methods for determination of vanadium and chromium in different materials.[41,43]

In some cases the carboxylic acids used as activators can affect simultaneously several stages of the catalytic reaction through a different mechanism.

Thus the oxidation of *p*-phenetidine with halates, catalysed by vanadium(V), is activated by citric acid. The activator acts in two stages of the reaction: it accelerates the catalyst–substrate interaction through a radical mechanism[40] [according to (13) and (14)] and at the same time increases the rate of regeneration of the catalyst, serving as a matrix for the $\mathrm{V(IV)–XO_3^-}$ interaction.[42]

Oxalic acid is also used as an activator for the same reaction, but while a strong effect on the catalyst–substrate interaction is observed,[40] at the same time it acts as an inhibitor for the regeneration of the catalyst.[32] The influence on the first, rate-limiting, stage of the process results in the rates of both reaction stages becoming of the same order and hence the inhibition of the second stage is now of importance. For that reason the total effect of oxalic acid on the overall reaction rate is smaller than that of citric acid.[44]

Another attempt at explanation of the difference in the effect of citric and oxalic acids on the rate-limiting stage and on the overall reaction rate was made by means of molecular orbital theory and the electronic spectra of the catalyst–activator complex.[45] Here the influence of the activator on the second reaction stage was not taken into account at all, the discussion including only the rate-determining step. It was shown that the energy of the charge-transfer band of the complex $M^{(n+1)+}$–A could be used to predict qualitatively the possibility of activation and the order of the activating effect in cases where the activator is oxidized during the reaction, according to (13).

Higher sensitivity is not the only advantage that could be realized by the use of activators in catalytic analysis. Another possibility seems much more attractive—selection of an activator for a given catalytic reaction, that would increase the catalytic activity of the ion to be determined and at the same time quench the activity of other catalysts that can interfere. In such a case an improvement in sensitivity and selectivity could be accomplished simultaneously.

Such a possibility was first pointed out and experimentally realized in 1963 in a catalytic method for determination of vanadium in the presence of copper(II) and iron(III), which also catalyse the indicator reaction.[46] The addition of citric acid increases the sensitivity for vanadium(V) by about 15 times, the activity of both interfering ions being completely suppressed.

The catalytic determination of silver offers another example. Thus 25 μg of silver can be determined catalytically by the sulphanilic acid oxidation, copper(II) and iron(III) interfering in amounts >0·6 μg and >10 μg respectively.[26] The use of 2,2′-dipyridyl permits the determination of 5×10^{-3} μg of silver (5000 times higher sensitivity) at the same time raising the levels at which copper(II) and iron(III) interfere to 10 and 100 μg respectively.[28] The presence of ethylenediamine increases the sensitivity for silver only 1000 times, but increases tolerance for copper(II) to 50 μg.[29]

It must be pointed out that so far only a few examples of simultaneous improvement of sensitivity and selectivity of catalytic reactions are known. In our opinion, however, this offers one of the most promising lines of research on application of activators in catalytic analysis.

The use of a combination of properly selected activators must also be mentioned as a prospective means of affecting a catalytic reaction. It was shown that sometimes the joint activating effect can be much higher than that of either activator alone.[47] Higher selectivity might also be expected, as shown by Kalinitchenko.[48] This work and other papers by the same author[49–51] are also interesting as examples of the use of activators in catalytic luminescence analysis. The simultaneous application of a system of activators is another promising field for research that could reveal new possibilities for further improvement of catalytic analytical methods.

CONCLUSION

The present paper does not pretend to cover all the data on activators and their application in catalytic analysis. Its aim is only to show the possibilities that the use of activators offers to the analyst, to discuss the mechanisms of their action and on that basis to show the way to select suitable activators for a given catalytic method. This, in our opinion, could help the further development and application of catalytic methods which are amongst the most sensitive modern analytical methods.

Zusammenfassung—Die Aktivierung der analytisch verwendeten homogenen katalytischen Reaktionen wird diskutiert. Die Verwendung von Aktivatoren bei katalytischen Methoden bringt einen Gewinn an Empfindlichkeit von 2–4 Größenordnungen und verbessert außerdem die Selektivität. Viele verschiedene Aktivierungsmechanismen werden diskutiert und als Beispiele für die Gesichtspunkte angeführt, nach denen man einen geeigneten Aktivator auswählt.

Résumé—On discute de l'activation de réactions catalytiques homogènes utilisées en analyse. L'emploi d'activeurs dans les méthodes catalytiques permet d'accroître leur sensibilité d'ordres de grandeur 2–4 et d'améliorer aussi bien leur sélectivité. On discute de nombreux mécanismes différents d'activation et les utilise comme illustration des principes pour le choix d'un activeur approprié.

REFERENCES

1. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, 2nd Ed., Khimia, Moscow, 1967; 1st Ed., Pergamon, Oxford, 1965.
2. T. Shiokawa and S. Suzuki, *J. Chem. Soc. Japan*, 1950, **71**, 629; *Chem. Abstr.*, 1951, **45**, 6538.
3. A. K. Babko and L V. Markova, *Zavodsk. Lab.*, 1959, **25**, 1283.
4. E. Michalski and A. Wtorkowska-Zaremba, *Acta Chim. Soc. Sci. Lodz.*, 1966, **11**, 45.
5. P. R. Bontchev and K. B. Yatsimirskii, *Theoret. Exp. Khim.*, 1965, **1**, 179.
6. P. R. Bontchev, G. Nikolov and B. Lilova, *Ann. Univ. Sofia (Khimia)*, 1964/65, **59**, 87.
7. K. B. Yatsimirskii, *Kinetics Catalysis (USSR)*, 1965, **4**, 931.
8. P. R. Bontchev and V. Michaylova, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2945.
9. P. R. Bontchev, N. D. Yordanov and V. Michaylova, *Z. Phys. Chem. Leipzig*, 1969, **242**, 408.
10. J. V. Rund and R. A. Plane, *J. Am. Chem. Soc.*, 1964, **86**, 367.
11. V. Michaylova, B. Evtimova and P. R. Bontchev, *Mikrochim. Acta*, 1968, 922.
12. V. Michaylova and P. R. Bontchev, *ibid.*, 1970, 344.
13. *Idem*, *ibid.*, 1970, 688.
14. P. R. Bontchev and B. G. Jeliazkova, *Inorg. Chim. Acta*, 1967, **1**, 249.
15. J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456; L. E. Orgel, *J. Inorg. Nucl. Chem.*, 1956, **2**, 137.
16. B. G. Jeliazkova, A. L. Tzvetanova and K. B. Yatsimirskii, *Zh. Analit. Khim.*, in the press.
17. P. R. Bontchev and K. Bontcheva, to be published.
18. H. Taube, *Can. J. Chem.*, 1959, **37**, 129.
19. M. Bobtelsky and B. Kirson, *Compt. Rend.*, 1934, **199**, 573.
20. N. Uri, *J. Phys. Colloid. Chem.*, 1949, **53**, 1070.
21. P. R. Bontchev, M. Miteva and B. G. Jeliazkova, *Inorg. Chim. Acta*, 1971, **5**, 75.
22. B. G. Jeliazkova and K. B. Yatsimirskii, *Theoret. Exp. Khim.*, 1972, in the press.
23. E. E. Kriss and K. B. Yatsimirskii, *Zh. Neorgan. Khim.*, 1971, **16**, 386.
24. R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
25. P. R. Bontchev and A. A. Alexiev, *Theoret. Exp. Khim.*, in the press.
26. A. A. Alexiev and P. R. Bontchev, *Mikrochim. Acta*, 1970, 13.
27. P. R. Bontchev and A. A. Alexiev, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2237.
28. P. R. Bontchev, A. A. Alexiev and B. Dimitrova, *Talanta*, 1969, **16**, 597.
29. P. R. Bontchev, A. A. Alexiev and I. Dimitrova, *Mikrochim. Acta*, 1970, 1104.
30. E. Yassinskene and E. Yankauskene, *Zh. Analit. Khim.*, 1966, **21**, 940.
31. E. Yassinskene and N. I. Rasevichute, *ibid.*, 1970, **25**, 458.
32. P. R. Bontchev and Z. Mladenova, *Mikrochim. Acta*, 1967, 427.
33. K. B. Yatsimirskii and V. E. Kalinina, *Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1965, **8**, 385.
34. P. R. Bontchev, *Ukr. Khim. Zh.*, 1964, **30**, 1167.
35. *Idem*, *Mikrochim. Acta*, 1962, 577.
36. S. Hünig and W. Daum, *Annalen*, 1955, **595**, 131.
37. L. K. J. Tong and M. C. Glesmann, *J. Am. Chem. Soc.*, 1968, **90**, 5164.
38. P. R. Bontchev and B. G. Jeliazkova, *Mikrochim. Acta*, 1967, 116.
39. P. R. Bontchev, unpublished results.
40. P. R. Bontchev and K. B. Yatsimirskii, *Zh. Fiz. Khim.*, 1965, **39**, 1995.
41. E. I. Yassinskene and E. B. Bilidene, *Zh. Analit. Khim.*, 1968, **23**, 143.
42. P. R. Bontchev and A. A. Alexiev, *Ukr. Khim. Zh.*, 1966, **32**, 1044.
43. V. M. Zyatkovskii, A. P. Filippov and K. B. Yatsimirskii, in *Methods of Analysis of Chemical Reagents*, 1966, No. 13, p. 69. IREA, Moscow, 1966.
44. P. R. Bontchev and A. A. Alexiev, *Ann. Univ. Sofia (Khimia)*, 1964/65, **59**, 77.
45. P. R. Bontchev and G. Nikolov, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2609.
46. P. R. Bontchev, *Mikrochim. Acta*, 1964, 79.
47. P. R. Bontchev and B. Evtimova, *ibid.*, 1968, 492.
48. I. E. Kalinitchenko, *Ukr. Khim. Zh.*, 1969, **35**, 755.
49. *Idem*, *ibid.*, 1968, **34**, 307.
50. A. K. Babko and I. E. Kalinitchenko, *ibid.*, 1965, **31**, 948.
51. *Idem*, *ibid.*, 1965, **31**, 1092.

Talanta, 1972, Vol. 19, pp. 687 to 688. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

N-Acetylacetone–anthranilic acid as a gravimetric reagent for copper(II)

(*Received* 25 *June* 1971. *Accepted* 18 *November* 1971)

METAL CHELATES of the Schiff bases have been recently reviewed by Holm *et al.*[1] Several metal chelates of the Schiff bases are solids and have therefore found application in gravimetry. No systematic study seems to have been made of the Schiff base *N*-acetylacetone–anthranilic acid (H_2AA). It is a diprotic tridentate ligand containing a carboxylic group, an enolic hydroxyl group and a donor nitrogen atom, which forms solid metal chelates with Fe(II), Co(II), Ni, Cu(II), Zn, Cd and UO_2(II).[2] The copper(II) chelate is insoluble in water, and can thus form the basis of a quantitative separation procedure.

EXPERIMENTAL

Reagents

N-Acetylacetone–anthranilic acid. The reagent was prepared by adding anthranilic acid (2·6 g) to freshly distilled acetylacetone (2·0 ml) and stirring thoroughly. Piperidine (2 or 3 drops) was used as a condensing agent. The mixture was refluxed on a water-bath for nearly an hour, till a transparent yellow solution was obtained. It was allowed to cool and then methanol was added and the solution was left overnight in a refrigerator for crystallization. Fine shining yellow crystals of the Schiff base were obtained which were separated, recrystallized from methanol and preserved in a vacuum desiccator. Yield 2·0 g. Found: C, 65·6%; H, 5·8%; N, 6·3%; calc. for $C_{12}H_{13}NO_3$: C, 65·75%, H, 5 93%; N, 6·36%.

Procedure

Gravimetric determination of copper(II). A 10% solution of the reagent was prepared in aqueous ethanol. Copper sulphate, 24·97 g, was dissolved in a litre of distilled water to give a copper(II) solution which was then standardized iodometrically.

An aliquot of the copper(II) solution was placed in a 250-ml Pyrex beaker and its pH was adjusted to between 3·9 and 4·6 with acetic acid–sodium acetate buffer. To this solution the reagent was added gradually with constant stirring till no further formation of the dark green precipitate took place. The contents of the flask were heated to 100° for 20 min, cooled and filtered (sintered glass crucible). The precipitate was wahed with warm aqueous alcohol till it was free from the reagent as well as sulphate. It was dried at 100°. Analyses gave: found, Cu, 22·6%; N, 4·0%; calc. for $Cu(C_{12}H_{11}NO_3)$, Cu, 22·64%; N, 4·99%. It has been found that nitrate, cobalt(II) and nickel(II) do not interfere in the estimation of copper(II) in the pH range 3·9–4·6.

The analysis of this chelate showed the metal–ligand ratio to be 1:1 and water to be absent. The molecular weight of the chelate in dioxan was found by ebulliometry to be 551 ± 15.

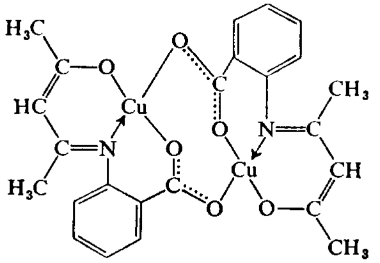
RESULTS AND DISCUSSION

The results of the gravimetric estimation of copper(II) by the procedure given earlier are summarized in Table I.

TABLE I.—RESULTS OF GRAVIMETRIC ESTIMATION OF COPPER(II)

Weight of chelate, *mg*	Copper, *mg* Found	Copper, *mg* Taken	Error, %
261·21	59·02	59·12	0·2
231·82	52·39	52·51	0·2
192·72	43·56	43·65	0·2
155·89	35·23	35·31	0·2
145·62	32·93	32·98	0·2

The copper(II) chelate exists as an unsolvated dimer, which is evident from its molecular weight. Infrared spectroscopy shows the absence of the characteristic frequencies of the —OH group in free or chelated form. Elemental analysis of the chelate reveals 1:1 metal–ligand ratio and also suggests the absence of water molecules. The magnetic moment was found to be 1·88 B.M. at 298 K. The electronic absorption spectra in dioxan and pyridine consist of two bands with peaks at 24000 and 14200 cm^{-1}, the first being the stronger. The band at 14200 cm^{-1} may be due to the electronic transition $2E \rightarrow 2T_2$ of the copper(II). The other band at 24600 cm^{-1} is an intraligand charge-transfer band. These results suggest a non-planar dimeric tetrahedral structure (I) for the copper(II) chelate. In this structure the four co-ordination positions of the cupric ions are fully satisfied and these ions are situated at the opposite ends of an eight-membered ring so that direct copper–copper bonding does not take place. Consequently superexchange is prevented and the chelate would exhibit a normal magnetic moment. Thus structure (I) explains satisfactorily all the experimental data. This structure is in agreement with that of the copper(II) complex of *N*-salicylidene–anthranilic acid investigated by Kubo *et al.*[3]



I

Acknowledgement—The authors are thankful to Prof. R. C. Kapoor, Head of Chemistry Department for providing necessary laboratory facilities.

Department of Chemistry
University of Jodhpur
Jodhpur India

R. K. Mehta
R. K. Gupta
S. L. Pania

Summary—*N*-Acetylacetone–anthranilic acid has been employed as a reagent for the gravimetric determination of copper(II). The solid copper(II) chelate formed possesses 1:1 metal–ligand stoichiometry and is found to exist as an unsolvated dimer. The complex has a magnetic moment of 1·88 B.M. at 298 K. A non-planar dimeric structure is suggested to explain the observed facts.

Zusammenfassung—*N*-Acetylaceton–anthranilsäure wurde als Reagens zur gravimetrischen Bestimmung von Kupfer(II) benutzt. Das gebildete feste Kupfer(II)-chelat besitzt die Stöchiometrie 1:1(Metall:Ligand) und liegt als unsolvatisiertes Dimeres vor. Der Komplex besitzt bei 298°K ein magnetisches Moment von 1,88 B.M. Zur Erklärung der Beobachtungen wird eine nichtebene Struktur des Dimeren vorgeschlagen.

Résumé—On a utilisé l'acide *N*-acétylacétone–anthranilique comme réactif pour le dosage gravimétrique du cuivre(II). Le chélate de cuivre(II) solide formé a une stoechiométrie métal–ligand 1:1 et l'on a trouvé qu'il existe comme dimère non solvaté. Le complexe a un moment magnétique de 1,88 B.M. à 298°K. On suggère une structure dimère non plane pour expliquer les faits observés.

REFERENCES

1. R. H. Holm, G. W. Everett Jr. and A. Chakravorty, *Progr. Inorg. Chem.*, Interscience, New York, 1966.
2. R. K. Mehta, R. K. Gupta and S. L. Pania, unpublished work.
3. M. Kubo, Y. Kuroda, M. Kishita and Y. Muto, *Austr. J. Chem.*, 1963, 7, 16.

Talanta, 1972, Vol. 19, pp. 687 to 688. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

N-Acetylacetone–anthranilic acid as a gravimetric reagent for copper(II)

(*Received* 25 *June* 1971. *Accepted* 18 *November* 1971)

METAL CHELATES of the Schiff bases have been recently reviewed by Holm *et al.*[1] Several metal chelates of the Schiff bases are solids and have therefore found application in gravimetry. No systematic study seems to have been made of the Schiff base *N*-acetylacetone–anthranilic acid (H_2AA). It is a diprotic tridentate ligand containing a carboxylic group, an enolic hydroxyl group and a donor nitrogen atom, which forms solid metal chelates with Fe(II), Co(II), Ni, Cu(II), Zn, Cd and UO_2(II).[2] The copper(II) chelate is insoluble in water, and can thus form the basis of a quantitative separation procedure.

EXPERIMENTAL

Reagents

N-Acetylacetone–anthranilic acid. The reagent was prepared by adding anthranilic acid (2·6 g) to freshly distilled acetylacetone (2·0 ml) and stirring thoroughly. Piperidine (2 or 3 drops) was used as a condensing agent. The mixture was refluxed on a water-bath for nearly an hour, till a transparent yellow solution was obtained. It was allowed to cool and then methanol was added and the solution was left overnight in a refrigerator for crystallization. Fine shining yellow crystals of the Schiff base were obtained which were separated, recrystallized from methanol and preserved in a vacuum desiccator. Yield 2·0 g. Found: C, 65·6%; H, 5·8%; N, 6·3%; calc. for $C_{12}H_{13}NO_3$: C, 65·75%, H, 5·93%; N, 6·36%.

Procedure

Gravimetric determination of copper(II). A 10% solution of the reagent was prepared in aqueous ethanol. Copper sulphate, 24·97 g, was dissolved in a litre of distilled water to give a copper(II) solution which was then standardized iodometrically.

An aliquot of the copper(II) solution was placed in a 250-ml Pyrex beaker and its pH was adjusted to between 3·9 and 4·6 with acetic acid–sodium acetate buffer. To this solution the reagent was added gradually with constant stirring till no further formation of the dark green precipitate took place. The contents of the flask were heated to 100° for 20 min, cooled and filtered (sintered glass crucible). The precipitate was wahed with warm aqueous alcohol till it was free from the reagent as well as sulphate. It was dried at 100°. Analyses gave: found, Cu, 22·6%; N, 4·0%; calc. for $Cu(C_{12}H_{11}NO_3)$, Cu, 22·64%; N, 4·99%. It has been found that nitrate, cobalt(II) and nickel(II) do not interfere in the estimation of copper(II) in the pH range 3·9–4·6.

The analysis of this chelate showed the metal–ligand ratio to be 1:1 and water to be absent. The molecular weight of the chelate in dioxan was found by ebulliometry to be 551 ± 15.

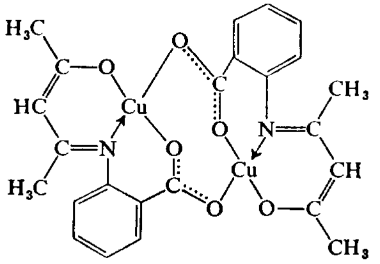
RESULTS AND DISCUSSION

The results of the gravimetric estimation of copper(II) by the procedure given earlier are summarized in Table I.

TABLE I.—RESULTS OF GRAVIMETRIC ESTIMATION OF COPPER(II)

Weight of chelate, *mg*	Copper, *mg* Found	Copper, *mg* Taken	Error, %
261·21	59·02	59·12	0·2
231·82	52·39	52·51	0·2
192·72	43·56	43·65	0·2
155·89	35·23	35·31	0·2
145·62	32·93	32·98	0·2

The copper(II) chelate exists as an unsolvated dimer, which is evident from its molecular weight. Infrared spectroscopy shows the absence of the characteristic frequencies of the —OH group in free or chelated form. Elemental analysis of the chelate reveals 1:1 metal–ligand ratio and also suggests the absence of water molecules. The magnetic moment was found to be 1·88 B.M. at 298 K. The electronic absorption spectra in dioxan and pyridine consist of two bands with peaks at 24000 and 14200 cm^{-1}, the first being the stronger. The band at 14200 cm^{-1} may be due to the electronic transition $2E \rightarrow 2T_2$ of the copper(II). The other band at 24600 cm^{-1} is an intraligand charge-transfer band. These results suggest a non-planar dimeric tetrahedral structure (I) for the copper(II) chelate. In this structure the four co-ordination positions of the cupric ions are fully satisfied and these ions are situated at the opposite ends of an eight-membered ring so that direct copper–copper bonding does not take place. Consequently superexchange is prevented and the chelate would exhibit a normal magnetic moment. Thus structure (I) explains satisfactorily all the experimental data. This structure is in agreement with that of the copper(II) complex of *N*-salicylidene–anthranilic acid investigated by Kubo *et al.*[3]



I

Acknowledgement—The authors are thankful to Prof. R. C. Kapoor, Head of Chemistry Department for providing necessary laboratory facilities.

Department of Chemistry
University of Jodhpur
Jodhpur India

R. K. MEHTA
R. K. GUPTA
S. L. PANIA

Summary—*N*-Acetylacetone–anthranilic acid has been employed as a reagent for the gravimetric determination of copper(II). The solid copper(II) chelate formed possesses 1:1 metal–ligand stoichiometry and is found to exist as an unsolvated dimer. The complex has a magnetic moment of 1·88 B.M. at 298 K. A non-planar dimeric structure is suggested to explain the observed facts.

Zusammenfassung—*N*-Acetylaceton–anthranilsäure wurde als Reagens zur gravimetrischen Bestimmung von Kupfer(II) benutzt. Das gebildete feste Kupfer(II)-chelat besitzt die Stöchiometrie 1:1(Metall:Ligand) und liegt als unsolvatisiertes Dimeres vor. Der Komplex besitzt bei 298°K ein magnetisches Moment von 1,88 B.M. Zur Erklärung der Beobachtungen wird eine nichtebene Struktur des Dimeren vorgeschlagen.

Résumé—On a utilisé l'acide *N*-acétylacétone–anthranilique comme réactif pour le dosage gravimétrique du cuivre(II). Le chélate de cuivre(II) solide formé a une stoechiométrie métal–ligand 1:1 et l'on a trouvé qu'il existe comme dimère non solvaté. Le complexe a un moment magnétique de 1,88 B.M. à 298°K. On suggère une structure dimère non plane pour expliquer les faits observés.

REFERENCES

1. R. H. Holm, G. W. Everett Jr. and A. Chakravorty, *Progr. Inorg. Chem.*, Interscience, New York, 1966.
2. R. K. Mehta, R. K. Gupta and S. L. Pania, unpublished work.
3. M. Kubo, Y. Kuroda, M. Kishita and Y. Muto, *Austr. J. Chem.*, 1963, 7, 16.

Talanta, 1972, Vol. 19, pp. 689 to 692. Pergamon Press. Printed in Northern Ireland

Analysis of metals by solid–liquid separation after liquid–liquid extraction
Spectrophotometric determination of palladium(II) by extraction of palladium dimethylglyoxime with melted naphthalene

(*Received* 9 *August* 1971. *Accepted* 15 *November* 1971)

RECENTLY many new reagents have been employed for the solvent extraction and spectrophotometric determination of small amounts of metal ions. We have been studying a new method "analysis by solid–liquid separation after liquid–liquid extraction," and this method has been successfully applied for the spectrophotometric determination of micro amounts of copper,[1,2] zinc,[3] magnesium[4] and nickel[5] by using a molten organic compound with appropriate melting point as the organic phase, *e.g.*, naphthalene (m.p. 80·1°), diphenyl (m.p. 70·5°) and a suitable organic reagent *e.g.*, 8 hydroxyquinoline or dimethyl glyoxime. Generally, the stable water-insoluble complexes are rapidly and quantitatively extracted into molten naphthalene, and micro amounts of metals can thus be determined with the same degree of accuracy as by chloroform extraction. The separation and drying of the naphthalene mixture after extraction takes longer than the comparable step in a simple chloroform extraction, but it is convenient for the determination of zinc, magnesium, cadmium, beryllium, *etc*, because the complexes of these metals are difficult to dissolve in chloroform or benzene. It is a characteristic of this method that the equilibrium distribution in the two phases is attained rapidly and the complexes are dissolved merely by contact with molten naphthalene.

In the present work, the extraction of palladium(II) with dimethylglyoxime into molten naphthalene is reported.

EXPERIMENTAL

Reagents

Standard palladium solution, $5 \times 10^{-3}M$. Prepared by dissolving 0·4433 g of palladium chloride in 10 ml of concentrated hydrochloric acid and diluting to 500 ml with water. More dilute palladium solutions were prepared as required by diluting the standard solution.

Dimethylglyoxime solution, 0·5% in ethanol.

Buffer solution. Appropriate mixtures of $1M$ acetic acid and $1M$ sodium acetate or, $0{\cdot}5M$ disodium hydrogen phosphate and $0{\cdot}5M$ potassium dihydrogen phosphate or $1M$ ammonia and $1M$ ammonium chloride.

Alkali metal salt solutions. Prepared by dissolving 1·000 g of each salt in water and diluting to 100 ml.

Solutions of metal salts. Made to contain 0·100 g of each salt per 100 ml of solution.

Naphthalene, chloroform and all other reagents were of analytical-reagent grade, and were used without further purification.

The water used was redistilled demineralized water.

Procedure

To 30 ml of the sample solution containing 1–9 ml of $5 \times 10^{-4}M$ palladium chloride, in a 50 or 100-ml tightly stoppered Erlenmeyer flask, add 2 ml of acetic acid–sodium acetate buffer solution and 1 ml of 0·5% dimethylglyoxime solution, and adjust the pH to about 4. Mix the solution well, and warm it on a water-bath at around 60°. Add 2·0 g of naphthalene and warm the mixture in the water-bath at 90° to melt the naphthalene layer completely. Shake it vigorously till the naphthalene layer solidifies. Once more melt and shake the mixture till the naphthalene layer solidifies, forming many very fine crystals, and allow to cool to room temperature. Again warm and melt the fine crystals slowly, and let them grow to give a coarser crystalline deposit. Cool to room temperature, collect the solidified deposit on a filter paper, wash with water, and blot the surplus water with a dry filter paper. Spread the crystals on a filter paper and allow to dry. Then dissolve them with chloroform by vigorous shaking and dilute to 10 ml. Dry the solution by addition of about 2 g of anhydrous sodium sulphate, transfer a portion into a 10-mm cell and measure its absorbance at 370 nm against a reagent blank prepared similarly. Calculate the amount of palladium from the calibration curve.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of dimethylglyoxime and palladium dimethylglyoximate in naphthalene–chloroform solution, measured against water, are shown in Fig. 1. Consideration of this led to 370 nm being adopted as the optimum wavelength.

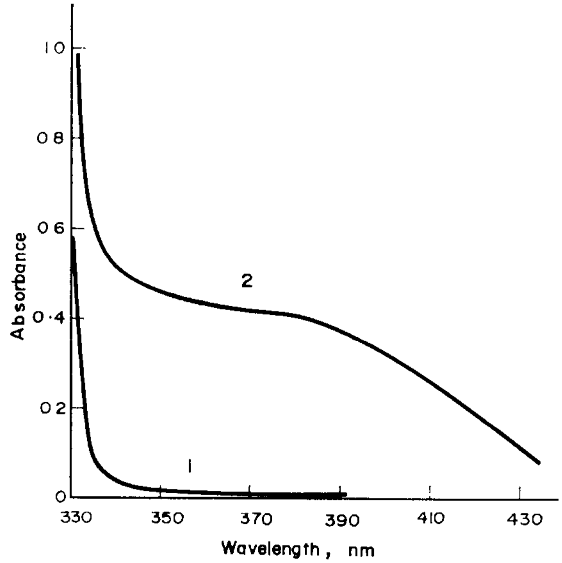


FIG. 1.—Absorption spectra of dimethylglyoxime and palladium dimethylglyoximate in naphthalene-chloroform.
Palladium: 266 μg; naphthalene: 2·0 g; pH: 4·0; 0·5% dimethylglyoxime: 1·0 ml; Reference: water; ① dimethylglyoxime; ② palladium dimethylglyoximate.

Effect of pH

The relationship between the absorbance and the pH of the aqueous solution after extraction was studied, and the results obtained are shown in Fig. 2. From these it is clear that the pH range 1·1–7·8 is suitable for quantitative extraction of palladium.

Effect of reagent concentration

The effect of dimethylglyoxime concentration on the absorbance was studied by varying the amount of dimethylglyoxime in solutions containing 266 μg of palladium at pH 4. The absorbance is maximal if 1·0 ml of 0·5% dimethylglyoxime solution is used, but varies by less than 1% over the range 0·5–3·0 ml.

Effect of amount of naphthalene

The amounts of naphthalene were varied from 0·5 to 2·8 g and the extraction was carried out by the recommended procedure. Only a slight increase in the absorbance was caused by increasing amounts of naphthalene. Large amounts of naphthalene made the experimental operations difficult owing to the sublimation of naphthalene, which was followed by the volatilization of chloroform. The volume of chloroform required to dissolve 1 g of naphthalene was 2 ml. Therefore, 2·0 g of naphthalene were used for further study.

Effect of concentration of buffer solution and shaking time

Sample solutions containing 266 μg of palladium, 1·0 ml of 0·5% dimethylglyoxime solution and various amounts of the acetate buffer solution in a total volume of about 33 ml were prepared according to the recommended procedure, and extracted with 2·0 g of naphthalene. The absorbance of the mixture of palladium complex and naphthalene in the chloroform solution was measured at 370 nm against the reagent blank. The amounts of the acetate buffer solution (pH 4) were varied from 0·5 to 4·5 ml at intervals of 0·5 ml. A negative error of 2% was found when 4·5 ml of the buffer

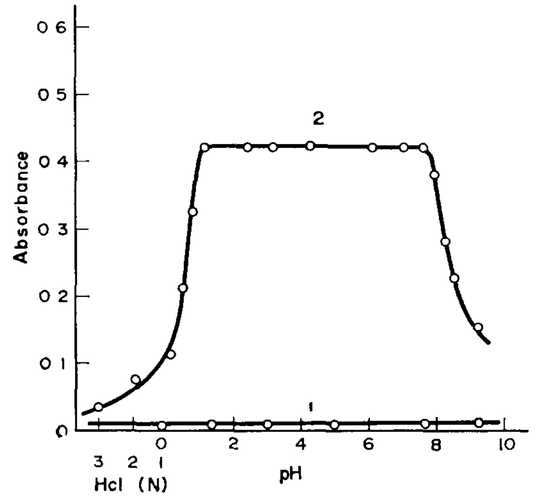


FIG. 2.—Effect of pH on absorbance.
Palladium: 266 μg; naphthalene: 2·0 g; wavelength: 370 nm; 0·5% dimethylglyoxime: 1·0 ml; Reference: water; ① dimethylglyoxime; ② palladium dimethylglyoximate.

solution were added. The extraction of the palladium complex into molten naphthalene was very fast owing to the high temperature; a constant degree of extraction was obtained when the vigorous shaking operation was repeated twice. Then the mixture of palladium complex and naphthalene had to be dissolved in chloroform by vigorous shaking because the solubility of the palladium complex in chloroform is rather low. The colour of the palladium complex in naphthalene–chloroform solution was quite stable for a long time.

Calibration curve

With the optimum conditions described above, the calibration curve for palladium determination was established at the wavelength of 370 nm against the reagent blank. It was linear over the range of 30–530 μg of palladium(II) in 10 ml of chloroform. The molar absorptivity was calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}, and the sensitivity 0·0626 μg of palladium per cm^2 for an absorbance of 0·001.

Sample solutions containing 266 μg of palladium, prepared by the recommended procedure, gave a mean absorbance of 0·425, with a standard deviation of 0·0027.

Effect of diverse ions

Various ions (100 mg of alkali metal salts or 1 mg of other salts) were added individually to solutions containing 266 μg of palladium, and their effects on the absorbance examined. The test solution was extracted with 2·0 g of naphthalene at a temperature above 81°. The following alkali metal salts and metal salts did not interfere: KSCN, $Na_2C_2O_4$, KH_2PO_4, Na_2HPO_4, Na_2CO_3, Na_2SO_3, NaF, KCl, KBr, KI, sodium tartrate, sodium citrate, EDTA, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, $Sr(NO_3)_2$, $BaCl_2$, $CdCl_2{\cdot}2\frac{1}{2}H_2O$, $Na_2WO_4{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$, $ZnCl_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Pb(NO_3)_2$, potassium alum, Mohr's salt. Nickel and iron(III) interfered seriously. Nickel did not interfere in the pH region 1·5–2·5. The interference of iron(III) was masked by addition of 10 ml of 1% EDTA or by reduction to iron(II) with 5 ml of 5% hydroxylamine sulphate solution.

TAITIRO FUJINAGA

Faculty of Science, Kyoto University
Sakyo-ku, Kyoto-shi

MASATADA SATAKE
TATSUO YONEKUBO

Faculty of Engineering, Fukui University
Fukui-shi, Japan

Summary—A method of liquid–liquid extraction of palladium dimethylglyoximate with molten naphthalene followed by solid–liquid separation is successfully applied to palladium. The complex between palladium and dimethylglyoxime is easily extracted into molten naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Zusammenfassung—Zur Bestimmung von Palladium wird Palladiumdimethylglyoximat mit geschmolzenem Naphthalin extrahiert und dann Festkörper und Flüssigkeit getrennt. Der Komplex aus Palladium und Dimethylglyoxim wird leicht in geschmolzenes Naphthalin extrahiert. Nach der Extraktion werden die sehr feinen Kristalle von wieder fest gewordenem Naphthalin in Chloroform gelöst und die Extinktion der Lösung bei 370 nm gegen eine Reagens-Blindprobe gemessen. Das Beersche Gesetz gilt bei 30–370 μg Palladium in 10 ml Chloroform, der molare Extinktionskoeffizient wird zu $1{,}72 \cdot 10^4$ 1 mol^{-1}mm^{-1} berechnet. Eine Reihe von Alkalimetallsalzen und Metallionen stören nicht. Die Störung durch Nickel(II) wird beseitigt, wenn bei pH 2 extrahiert wird, die durch Eisen(III) durch Maskierung mit EDTA oder durch Reduktion zu Eisen(II). Die Methode ist schnell und genau.

Résumé—On a appliqué avec succès au palladium une méthode d'extraction liquide-liquide du diméthylglyoximate de palladium avec du naphtalène fondu, suivie d'une séparation solide-liquide. Le complexe entre le palladium et la diméthylglyoxime est aisément extrait en naphtalène fondu. Après extraction, les cristaux très fins de naphtalène solidifié sont dissous en chloroforme, et l'on mesure l'absorption de la solution résultante à 370 nm par rapport à un témoin des réactifs. La loi de Beer est suivie pour 30–370 μg de palladium dans 10 ml de chloroforme, et l'on a calculé que le coefficient d'absorption moléculaire est de $1{,}72 \times 10^4$ mm^{-1} l.mole^{-1}. Divers sels alcalins et ions métalliques ne gênent pas. On évite l'interférence du nickel(II) par l'extraction à pH 2, et celle du fer(III) en le dissimulant par l'EDTA ou par réduction en fer(II). La méthode est rapide et précise.

REFERENCES

1. T. Fujinaga, T. Kuwamoto and E. Nakayama, *Talanta*, 1969, **16**, 1225.
2. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *Bunseki Kagaku*, 1969, **18**, 1113.
3. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 217.
4. M. Satake, *Memoirs Fac. Engineering, Fukui University*, 1970, **18**, 225.
5. T. Fujinaga, M. Satake and T. Yonekubo, *Bunseki Kagaku*, in the press.

Talanta, 1972, Vol. 19, pp. 692 to 695. Pergamon Press. Printed in Northern Ireland

Détermination gravimétrique de l'iode sous forme de Nt(ICl$_2$)*

(*Reçu le* 28 *avril* 1971. *Accepté le* 28 *novembre* 1971)

On connaît deux méthodes de détermination gravimétrique de l'iode. Elles sont basées sur sa précipitation sous forme d'AgI[1] et d'iodure de palladium(II).[2] Une méthode gravimétrique de détermination de l'iode sous forme d'un autre composé, utilisant un agent organique, n'a pas été proposée jusqu'ici. C'est une telle méthode que nous préconisons dans le présent mémoire. L'iode y est déterminé et pesé sous forme de dichloriodure de nitron.

* L'abréviation Nt désigne le cation de la base (nitron).

Talanta, 1972, Vol. 19, pp. 689 to 692. Pergamon Press. Printed in Northern Ireland

Analysis of metals by solid–liquid separation after liquid–liquid extraction
Spectrophotometric determination of palladium(II) by extraction of palladium dimethylglyoximate with melted naphthalene

(*Received* 9 *August* 1971. *Accepted* 15 *November* 1971)

RECENTLY many new reagents have been employed for the solvent extraction and spectrophotometric determination of small amounts of metal ions. We have been studying a new method "analysis by solid–liquid separation after liquid–liquid extraction," and this method has been successfully applied for the spectrophotometric determination of micro amounts of copper,[1,2] zinc,[3] magnesium[4] and nickel[5] by using a molten organic compound with appropriate melting point as the organic phase, *e.g.*, naphthalene (m.p. 80·1°), diphenyl (m.p. 70·5°) and a suitable organic reagent *e.g.*, 8 hydroxyquinoline or dimethyl glyoxime. Generally, the stable water-insoluble complexes are rapidly and quantitatively extracted into molten naphthalene, and micro amounts of metals can thus be determined with the same degree of accuracy as by chloroform extraction. The separation and drying of the naphthalene mixture after extraction takes longer than the comparable step in a simple chloroform extraction, but it is convenient for the determination of zinc, magnesium, cadmium, beryllium, *etc*, because the complexes of these metals are difficult to dissolve in chloroform or benzene. It is a characteristic of this method that the equilibrium distribution in the two phases is attained rapidly and the complexes are dissolved merely by contact with molten naphthalene.

In the present work, the extraction of palladium(II) with dimethylglyoxime into molten naphthalene is reported.

EXPERIMENTAL

Reagents

Standard palladium solution, $5 \times 10^{-3}M$. Prepared by dissolving 0·4433 g of palladium chloride in 10 ml of concentrated hydrochloric acid and diluting to 500 ml with water. More dilute palladium solutions were prepared as required by diluting the standard solution.

Dimethylglyoxime solution, 0·5% in ethanol.

Buffer solution. Appropriate mixtures of $1M$ acetic acid and $1M$ sodium acetate or, $0{\cdot}5M$ disodium hydrogen phosphate and $0{\cdot}5M$ potassium dihydrogen phosphate or $1M$ ammonia and $1M$ ammonium chloride.

Alkali metal salt solutions. Prepared by dissolving 1·000 g of each salt in water and diluting to 100 ml.

Solutions of metal salts. Made to contain 0·100 g of each salt per 100 ml of solution.

Naphthalene, chloroform and all other reagents were of analytical-reagent grade, and were used without further purification.

The water used was redistilled demineralized water.

Procedure

To 30 ml of the sample solution containing 1–9 ml of $5 \times 10^{-4}M$ palladium chloride, in a 50 or 100-ml tightly stoppered Erlenmeyer flask, add 2 ml of acetic acid–sodium acetate buffer solution and 1 ml of 0·5% dimethylglyoxime solution, and adjust the pH to about 4. Mix the solution well, and warm it on a water-bath at around 60°. Add 2·0 g of naphthalene and warm the mixture in the water-bath at 90° to melt the naphthalene layer completely. Shake it vigorously till the naphthalene layer solidifies. Once more melt and shake the mixture till the naphthalene layer solidifies, forming many very fine crystals, and allow to cool to room temperature. Again warm and melt the fine crystals slowly, and let them grow to give a coarser crystalline deposit. Cool to room temperature, collect the solidified deposit on a filter paper, wash with water, and blot the surplus water with a dry filter paper. Spread the crystals on a filter paper and allow to dry. Then dissolve them with chloroform by vigorous shaking and dilute to 10 ml. Dry the solution by addition of about 2 g of anhydrous sodium sulphate, transfer a portion into a 10-mm cell and measure its absorbance at 370 nm against a reagent blank prepared similarly. Calculate the amount of palladium from the calibration curve.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of dimethylglyoxime and palladium dimethylglyoximate in naphthalene–chloroform solution, measured against water, are shown in Fig. 1. Consideration of this led to 370 nm being adopted as the optimum wavelength.

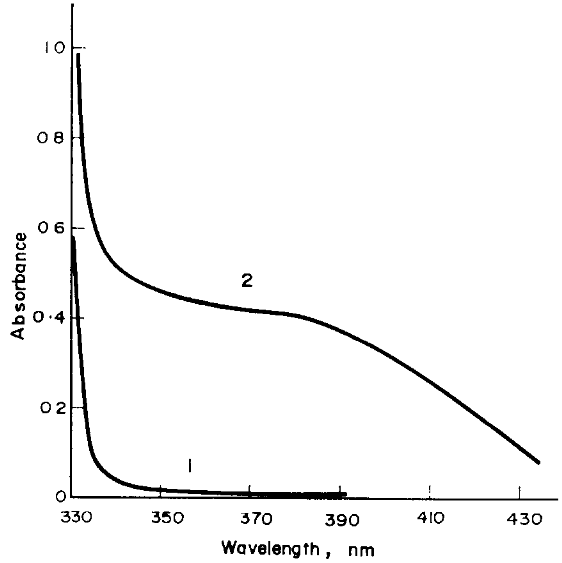


Fig. 1.—Absorption spectra of dimethylglyoxime and palladium dimethylglyoximate in naphthalene-chloroform.
Palladium: 266 μg; naphthalene: 2·0 g; pH: 4·0; 0·5% dimethylglyoxime: 1·0 ml; Reference: water; ① dimethylglyoxime; ② palladium dimethylglyoximate.

Effect of pH

The relationship between the absorbance and the pH of the aqueous solution after extraction was studied, and the results obtained are shown in Fig. 2. From these it is clear that the pH range 1·1–7·8 is suitable for quantitative extraction of palladium.

Effect of reagent concentration

The effect of dimethylglyoxime concentration on the absorbance was studied by varying the amount of dimethylglyoxime in solutions containing 266 μg of palladium at pH 4. The absorbance is maximal if 1·0 ml of 0·5% dimethylglyoxime solution is used, but varies by less than 1% over the range 0·5–3·0 ml.

Effect of amount of naphthalene

The amounts of naphthalene were varied from 0·5 to 2·8 g and the extraction was carried out by the recommended procedure. Only a slight increase in the absorbance was caused by increasing amounts of naphthalene. Large amounts of naphthalene made the experimental operations difficult owing to the sublimation of naphthalene, which was followed by the volatilization of chloroform. The volume of chloroform required to dissolve 1 g of naphthalene was 2 ml. Therefore, 2·0 g of naphthalene were used for further study.

Effect of concentration of buffer solution and shaking time

Sample solutions containing 266 μg of palladium, 1·0 ml of 0·5% dimethylglyoxime solution and various amounts of the acetate buffer solution in a total volume of about 33 ml were prepared according to the recommended procedure, and extracted with 2·0 g of naphthalene. The absorbance of the mixture of palladium complex and naphthalene in the chloroform solution was measured at 370 nm against the reagent blank. The amounts of the acetate buffer solution (pH 4) were varied from 0·5 to 4·5 ml at intervals of 0·5 ml. A negative error of 2% was found when 4·5 ml of the buffer

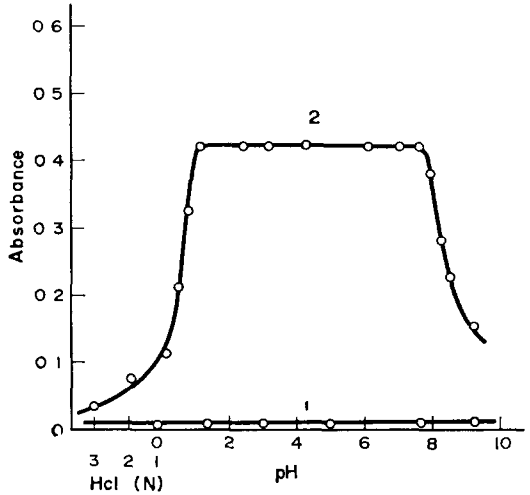


FIG. 2.—Effect of pH on absorbance.
Palladium: 266 μg; naphthalene: 2·0 g; wavelength: 370 nm; 0·5% dimethylglyoxime: 1·0 ml; Reference: water; ① dimethylglyoxime; ② palladium dimethylglyoximate.

solution were added. The extraction of the palladium complex into molten naphthalene was very fast owing to the high temperature; a constant degree of extraction was obtained when the vigorous shaking operation was repeated twice. Then the mixture of palladium complex and naphthalene had to be dissolved in chloroform by vigorous shaking because the solubility of the palladium complex in chloroform is rather low. The colour of the palladium complex in naphthalene-chloroform solution was quite stable for a long time.

Calibration curve

With the optimum conditions described above, the calibration curve for palladium determination was established at the wavelength of 370 nm against the reagent blank. It was linear over the range of 30–530 μg of palladium(II) in 10 ml of chloroform. The molar absorptivity was calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}, and the sensitivity 0·0626 μg of palladium per cm^2 for an absorbance of 0·001.

Sample solutions containing 266 μg of palladium, prepared by the recommended procedure, gave a mean absorbance of 0·425, with a standard deviation of 0·0027.

Effect of diverse ions

Various ions (100 mg of alkali metal salts or 1 mg of other salts) were added individually to solutions containing 266 μg of palladium, and their effects on the absorbance examined. The test solution was extracted with 2·0 g of naphthalene at a temperature above 81°. The following alkali metal salts and metal salts did not interfere: KSCN, $Na_2C_2O_4$, KH_2PO_4, Na_2HPO_4, Na_2CO_3, Na_2SO_3, NaF, KCl, KBr, KI, sodium tartrate, sodium citrate, EDTA, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, $Sr(NO_3)_2$, $BaCl_2$, $CdCl_2{\cdot}2\frac{1}{2}H_2O$, $Na_2WO_4{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$, $ZnCl_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Pb(NO_3)_2$, potassium alum, Mohr's salt. Nickel and iron(III) interfered seriously. Nickel did not interfere in the pH region 1·5–2·5. The interference of iron(III) was masked by addition of 10 ml of 1% EDTA or by reduction to iron(II) with 5 ml of 5% hydroxylamine sulphate solution.

TAITIRO FUJINAGA

Faculty of Science, Kyoto University
Sakyo-ku, Kyoto-shi

MASATADA SATAKE
TATSUO YONEKUBO

Faculty of Engineering, Fukui University
Fukui-shi, Japan

Summary—A method of liquid-liquid extraction of palladium dimethylglyoximate with molten naphthalene followed by solid-liquid separation is successfully applied to palladium. The complex between palladium and dimethylglyoxime is easily extracted into molten naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Zusammenfassung—Zur Bestimmung von Palladium wird Palladiumdimethylglyoximat mit geschmolzenem Naphthalin extrahiert und dann Festkörper und Flüssigkeit getrennt. Der Komplex aus Palladium und Dimethylglyoxim wird leicht in geschmolzenes Naphthalin extrahiert. Nach der Extraktion werden die sehr feinen Kristalle von wieder fest gewordenem Naphthalin in Chloroform gelöst und die Extinktion der Lösung bei 370 nm gegen eine Reagens-Blindprobe gemessen. Das Beersche Gesetz gilt bei 30–370 μg Palladium in 10 ml Chloroform, der molare Extinktionskoeffizient wird zu $1{,}72 \cdot 10^4$ l mol^{-1}mm^{-1} berechnet. Eine Reihe von Alkalimetallsalzen und Metallionen stören nicht. Die Störung durch Nickel(II) wird beseitigt, wenn bei pH 2 extrahiert wird, die durch Eisen(III) durch Maskierung mit EDTA oder durch Reduktion zu Eisen(II). Die Methode ist schnell und genau.

Résumé—On a appliqué avec succès au palladium une méthode d'extraction liquide-liquide du diméthylglyoximate de palladium avec du naphtalène fondu, suivie d'une séparation solide-liquide. Le complexe entre le palladium et la diméthylglyoxime est aisément extrait en naphtalène fondu. Après extraction, les cristaux très fins de naphtalène solidifié sont dissous en chloroforme, et l'on mesure l'absorption de la solution résultante à 370 nm par rapport à un témoin des réactifs. La loi de Beer est suivie pour 30–370 μg de palladium dans 10 ml de chloroforme, et l'on a calculé que le coefficient d'absorption moléculaire est de $1{,}72 \times 10^4$ mm^{-1} l.mole^{-1}. Divers sels alcalins et ions métalliques ne gênent pas. On évite l'interférence du nickel(II) par l'extraction à pH 2, et celle du fer(III) en le dissimulant par l'EDTA ou par réduction en fer(II). La méthode est rapide et précise.

REFERENCES

1. T. Fujinaga, T. Kuwamoto and E. Nakayama, *Talanta*, 1969, **16**, 1225.
2. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *Bunseki Kagaku*, 1969, **18**, 1113.
3. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 217.
4. M. Satake, *Memoirs Fac. Engineering, Fukui University*, 1970, **18**, 225.
5. T. Fujinaga, M. Satake and T. Yonekubo, *Bunseki Kagaku*, in the press.

Talanta, 1972, Vol. 19, pp. 692 to 695. Pergamon Press. Printed in Northern Ireland

Détermination gravimétrique de l'iode sous forme de $Nt(ICl_2)$*

(*Reçu le* 28 *avril* 1971. *Accepté le* 28 *novembre* 1971)

On connaît deux méthodes de détermination gravimétrique de l'iode. Elles sont basées sur sa précipitation sous forme d'AgI[1] et d'iodure de palladium(II).[2] Une méthode gravimétrique de détermination de l'iode sous forme d'un autre composé, utilisant un agent organique, n'a pas été proposée jusqu'ici. C'est une telle méthode que nous préconisons dans le présent mémoire. L'iode y est déterminé et pesé sous forme de dichloriodure de nitron.

* L'abréviation Nt désigne le cation de la base (nitron).

naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Zusammenfassung—Zur Bestimmung von Palladium wird Palladiumdimethylglyoximat mit geschmolzenem Naphthalin extrahiert und dann Festkörper und Flüssigkeit getrennt. Der Komplex aus Palladium und Dimethylglyoxim wird leicht in geschmolzenes Naphthalin extrahiert. Nach der Extraktion werden die sehr feinen Kristalle von wieder fest gewordenem Naphthalin in Chloroform gelöst und die Extinktion der Lösung bei 370 nm gegen eine Reagens-Blindprobe gemessen. Das Beersche Gesetz gilt bei 30–370 μg Palladium in 10 ml Chloroform, der molare Extinktionskoeffizient wird zu $1{,}72 \cdot 10^4$ 1 mol^{-1}mm^{-1} berechnet. Eine Reihe von Alkalimetallsalzen und Metallionen stören nicht. Die Störung durch Nickel(II) wird beseitigt, wenn bei pH 2 extrahiert wird, die durch Eisen(III) durch Maskierung mit EDTA oder durch Reduktion zu Eisen(II). Die Methode ist schnell und genau.

Résumé—On a appliqué avec succès au palladium une méthode d'extraction liquide-liquide du diméthylglyoximate de palladium avec du naphtalène fondu, suivie d'une séparation solide-liquide. Le complexe entre le palladium et la diméthylglyoxime est aisément extrait en naphtalène fondu. Après extraction, les cristaux très fins de naphtalène solidifié sont dissous en chloroforme, et l'on mesure l'absorption de la solution résultante à 370 nm par rapport à un témoin des réactifs. La loi de Beer est suivie pour 30–370 μg de palladium dans 10 ml de chloroforme, et l'on a calculé que le coefficient d'absorption moléculaire est de $1{,}72 \times 10^4$ mm^{-1} l.mole^{-1}. Divers sels alcalins et ions métalliques ne gênent pas. On évite l'interférence du nickel(II) par l'extraction à pH 2, et celle du fer(III) en le dissimulant par l'EDTA ou par réduction en fer(II). La méthode est rapide et précise.

REFERENCES

1. T. Fujinaga, T. Kuwamoto and E. Nakayama, *Talanta*, 1969, **16**, 1225.
2. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *Bunseki Kagaku*, 1969, **18**, 1113.
3. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 217.
4. M. Satake, *Memoirs Fac. Engineering, Fukui University*, 1970, **18**, 225.
5. T. Fujinaga, M. Satake and T. Yonekubo, *Bunseki Kagaku*, in the press.

Talanta, 1972, Vol. 19, pp. 692 to 695. Pergamon Press. Printed in Northern Ireland

Détermination gravimétrique de l'iode sous forme de Nt(ICl$_2$)*

(*Reçu le* 28 *avril* 1971. *Accepté le* 28 *novembre* 1971)

On connaît deux méthodes de détermination gravimétrique de l'iode. Elles sont basées sur sa précipitation sous forme d'AgI[1] et d'iodure de palladium(II).[2] Une méthode gravimétrique de détermination de l'iode sous forme d'un autre composé, utilisant un agent organique, n'a pas été proposée jusqu'ici. C'est une telle méthode que nous préconisons dans le présent mémoire. L'iode y est déterminé et pesé sous forme de dichloriodure de nitron.

* L'abréviation Nt désigne le cation de la base (nitron).

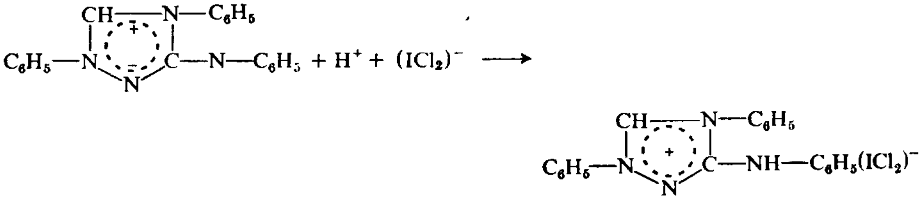
Des essais[3] portant sur le système eau–acide chlorhydrique–iode–chlore, ont montré que lors de son oxydation au moyen du chlore en milieu chlorhydrique saturé de chlore, l'iode se transforme quantitativement en complex $(ICl_2)^-$. On sait que les anions de même type $(ICl_4)^-$ et $(AuCl_4)^-$ réagissant avec certaines bases organique, fournissent des composés peu solubles et que les méthodes de détermination quantitative de la nicotine[4] et de l'or[5] sont basées sur ces propriétés. Ayant en vue ces faits, nous nous sommes proposés pour but d'élaborer une nouvelle méthode gravimétrique de détermination de l'iode, où seraient mises à profit les propriétés du composé que forme le complexe $(ICl_2)^-$ avec le nitron.

PARTIE EXPERIMENTALE

Si l'on additionne une solution contenant le complexe (ICl_2) d'une solution de sulphate de nitron, on obtient un précipité faiblement coloré en jaune qui, après agitation, acquiert une forme nettement cristalline.

Le composé s'obtient en milieu chlorhydrique fortement saturé (d'acide chlorhydrique) offre une solubilité extrêmement faible.

La réaction entre le nitron et le complexe $(ICl_2)^-$ se déroule probablement selon l'équation suivante:



La basicité élevée du nitron provoque la production de protons et l'association du nitron et du complexe iodochlorure. Ce mécanisme se trouve confirmé par les spectres IR du composé obtenu et du nitron. Le spectre du composé, contrairement à celui du nitron, présente un pic de liaison N–H nettement visible.

On a procédé à l'analyse du composé pour en déterminer les teneurs en C, H, N, et la somme de l'iode et du chlore. Les résultats figurent dans le tableau No. I. On y inclu aussi les résultats théoriques, calculés selon les formules: $Nt(ICl_2)$, $Nt(ICl_4)$. Les données du tableau attestent que le composé obtenu est $Nt(ICl_2)$.

Tableau I.—Données sur la constitution du composé

	C%	H%	N%	Cl + I%
Théorie pour $Nt(ICl_2)$	47,06	3,34	10,98	38,82
Trouvé	47,4	3,5	10,2	38,6
Théorie pour $Nt(ICl_4)$	43,08	2,95	9,66	46,38

$Nt(ICl_2)$ fond sans se décomposer à 160°C. Il se dissout au mieux dans l'acétone, moins bien dans l'alcool éthylique (0,74%), le dichloréthane (0,40%), le chloroforme (0,06%) et l'éther (0,04%). Il est insoluble dans les solvants non-polaires: benzène, tétrachloromethane. Dans l'eau le composé acquiert une coloration orangée qui, en fin d'opération, vire au noire. Sa solubilité a été déterminée en HCl à 5%, où il ne manifeste pas de modification.

À la température de 20°C, en HCl à 5%, la solubilité est de $6,3 \times 10^{-5}M$ en HCl à 5% et en présence de sulfate de nitron que nous avons basé notre nouvelle méthode gravimétrique de détermination de l'iode.

Analyse

Dans un ballon Kjeldahl de 50 ml on introduit environ 20 ml de solution d'ions iodiques contenant de 5 à 40 mg d'iode. On ajoute 20 ml de HCl concentré, saturé en Cl_2, agite, et, aussitôt, on fait barboter de l'air durant 5 minutes à travers cette solution. On transvase le mélange dans une fiole et le dilue à 100 ml, puis on ajoute lentement, et en agitant toujours, 25 ml de solution de sulfate de nitron à 1%. On obtient d'abord un précipité jaune à peine perceptible qui, après agitation énergique, acquiert peu à peu une coloration jaune et une structure cristalline très nette. On laisse reposer pendant une heure, puis on filtre sur un filtre de verre G_3 ou G_4.

Le contenu de la fiole est versé sur le filtre, puis la fiole est rincée par de l'acide chlorhydrique à 4% contenant un peu de sulfate de nitron où, mieux encore, par le filtrat lui-même. Le précipité est ensuite lavé à deux où trois reprises par un peu d'acide chlorhydrique à 4%, sêché pendant 1 hr à 100°–105° et pesé.

Pour illustrer la précision de la méthode, nous avons établi le tableau No. II, qui rend compte des résultats relatifs aux quantités de 4,5 à 40 mg.

Le coefficient de variation pour 15 à 40 mg dans 10 déterminations, evalué pour une sûreté statistique de 95% est respectivement de ±1,70 et ±0,75%.

TABLEAU II.—DETERMINATION DE L'IODE AVEC NITRON

Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %
4,5	4,34	−3,5	15,0	$15,0_6$	+0,4	40,0	$39,8_5$	−0,4
4,5	4,34	−3,5	15,0	$14,9_4$	−0,4	40,0	$39,8_0$	−0,5
4,5	4,39	−2,2	15,0	$14,7_8$	−1,5	40,0	$39,8_0$	−0,5
4,5	4,34	−3,5	15,0	$15,0_8$	+0,5	40,0	$40,0_7$	−0,2
—	—	—	15,0	$15,0_6$	+0,4	40,0	$39,9_7$	−0,1
—	—	—	15,0	$15,0_8$	+0,5	40,0	$39,9_4$	−0,2
—	—	—	15,0	$14,8_8$	−0,8	40,0	$40,2_5$	+0,6
—	—	—	15,0	$15,0_4$	+0,3	40,0	$40,0_0$	±0,0
—	—	—	15,0	$15,0_3$	+0,5	40,0	$39,8_5$	−0,1
—	—	—	15,0	$14,8_1$	−1,3	40,0	$39,8_2$	−0,5
Erreur relat. moyenne		−3,2%			−0,1%			−0,2%

Les ions bromate ne gênent pas la détermination. Si leur quantité est de l'ordre de celle de l'iode, il n'est pas indispensable de changer de mode opératoire. En l'occurence, lors du barbotage, le brome obtenu est éliminé en même temps que l'excédent de chlore, ce qui modifie pas les conditions du travail ultérieur. Si la teneur en Br est élevée, par example si le rapport Br/I = 5–10 et même davantage, la technique doit être modifiée en début d'opération. Dans le ballon de Kjeldahl on doit introduire d'abord de l'acide chlorhydrique concentré et saturé en chlore, puis remplir le ballon de chlore et, alors seulement ajouter à l'aide d'une pipette la solution à analyser. Par la suite, la détermination se déroule selon le schéma décrit plus haut. Dans ces conditions la présence du Br n'a pas d'effet sur les résultats. Ainsi, dans deux déterminations de 40 mg d'I, en présence de la même quantité de Br, on a détecté 40,10 et 40,15 mg d'iode.

La méthode préconisée a été confrontée avec la méthode la plus sûre, pratiquée le plus souvent la détermination gravimétrique de l'iode, sous forme d'AgI. Les résultats de 10 essais de détermination de 15 et de 40 mg d'iode, effectués avec précipitation par l'argent, figurement dans le tableau No. III. La confrontation des données des tableaux II et III, met en évidence d'une façon catégorique la meilleure précision de la nouvelle méthode. Elle présente encore les avantages suivants.

1. Elle se déroule en présence de Cl et de Br.
2. Elle exclu l'erreur due à l'oxydation de I^- en I_2.
3. La décomposition d'AgI, sous l'effet de la lumière n'entrâine pas d'erreurs.
4. Contrairement au précipité d'AgI, celui de $Nt(ICl_2)$ ne retient pas de solvant ni d'autres substances contenues dans la solution.

TABLEAU III.—DETERMINATION DE L'IODE AVEC L'ARGENT

Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %
15,0	$15,1_6$	+1,1	40,0	40,6	+1,5
15,0	$15,1_6$	+1,1	40,0	40,7	+1,8
15,0	$15,7_1$	+4,7	40,0	40,2	+0,5
15,0	$15,4_3$	+2,8	40,0	39,9	−0,3
15,0	$15,4_8$	+3,2			
15,0	$15,4_8$	+3,0			
Erreur relative moyenne		+2,6%			+0,9%

5. En raison du poids moléculaire élevé et de la faible solubilité de Nt(ICl$_2$), la méthode permet de déterminer des quantités d'iode 2–3 fois plus petites.

6. Pour la même raison, le facteur de transformation du poids du précipité en iode est aussi deux fois plus petit.

7. On utilise le sulfate et non pas l'acétate de nitron, car le nitron, comme reactif, contient beaucoup d'impurités qui, au cours de sa dissolution dans l'acide acétique, restent dans la solution et empêchent la détermination. Au contraire, le sulphate peut être facilement obtenu du nitron.[6]

N. Gantchev
V. Kanazirska
D. Athanassova

Chaire de chimie analytique
Ecole Normale Superieure
7 rue "V. Markov", Plovdiv, Bulgarie

Résumé—On a obtenu le composé dichloriodure de nitron—Nt(ICl$_2$)—et l'on a etudié les propriétés. En se basant sur les résultats obtenus, on a elaboré une méthode gravimétrique de détermination de l'iode sous forme de Nt(ICl$_2$). Elle permet de determiner par voie gravimétrique de 4 à 40 mg d'iode, l'erreur étant moindre que lors de détermination de l'iode sous forme d'AgI. Les ions bromate et chlorate ne gênent pas la détermination.

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

Zusammenfassung—Nitrondichlorojodid—Nt(JCl$_2$)—wurde hergestellt und untersucht; auf den Ergebnissen wurde eine gravimetrische Bestimmung von Jod als Nt(JCl$_2$) aufgebaut. Für 4–40 mg Jod ist der Fehler kleiner als bei der Bestimmung als AgJ. Bromat und Chlorat stören nicht.

BIBLIOGRAPHIE

1. W. F. Hillebrand, G. E. F. Lundell, H. I. Bright et J. A. Hoffman, *Applied Inorganic Analysis*, (*Russian Edition*), p. 816, 1966.
2. R. Streibinger et J. Pollak, *Microchemie*, 1925, **3**, 38.
3. N. Gantchev et D. Athanassova, *Trav. Sci.*, *Ecole Normale Superieure*, *Plovdiv* 1972, 2.
4. F. D. Chattaway et G. D. Parkes, *J. Chem. Soc.*, 1929, 1314.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Ukr. Akad. Nauk.*, 1970, **36**, 1184.
6. A. S. Babenko, V. N. Tolmatchev et A. N. Didzin, *Ukr. Khim. Zh.*, 1963, **29**, 702.

Talanta, 1972, Vol. 19, pp. 695 to 697. Pergamon Press. Printed in Northern Ireland

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten

(*Eingegangen am* 19. *Juli* 1971. *Angenommen am* 18. *Oktober* 1971)

Die analytische Chemie der Phosphate gewinnt auf Grund der vielfältigen Formen und des häufigen Auftretens dieser Verbindungen in Natur- und Syntheseprodukten zunehmend an Bedeutung. Bisherige papierchromatographische[1,2] und dünnschicht-chromatographische Trennungen (an Celluloseschichten)[3] zeigen zwar gute Ergebnisse, sind aber nur schwer reproduzierbar. Im Gegensatz dazu liefert die Gradientenelution an Anionenaustauscher-Säulen[4,5] sehr gute Ergebnisse, jedoch ist dieses Verfahren sehr zeitaufwendig. Um die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches zu verbinden, wendeten wir die Ionenaustauscher-Dünnschichtchromatographie an.[6,7] Wir verwendeten selbst gefertigte Anionenaustauscher-Fertigplatten (200 × 200 mm) vom Typ Dowex 2-X8, die sowohl in der Chlorid-, als auch in der Acetat-Form vorlagen. Zum Vergleich wurden auch einige "Ionex 25" Anionenaustauscher-Fertigplatten des gleichen Typs der Firma Macherey-Nagel (Düren, BRD) in der Acetat-Form herangezogen.

naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1{\cdot}72 \times 10^4$ l.mole.$^{-1}$mm^{-1}. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Zusammenfassung—Zur Bestimmung von Palladium wird Palladiumdimethylglyoximat mit geschmolzenem Naphthalin extrahiert und dann Festkörper und Flüssigkeit getrennt. Der Komplex aus Palladium und Dimethylglyoxim wird leicht in geschmolzenes Naphthalin extrahiert. Nach der Extraktion werden die sehr feinen Kristalle von wieder fest gewordenem Naphthalin in Chloroform gelöst und die Extinktion der Lösung bei 370 nm gegen eine Reagens-Blindprobe gemessen. Das Beersche Gesetz gilt bei 30–370 μg Palladium in 10 ml Chloroform, der molare Extinktionskoeffizient wird zu $1{,}72 \cdot 10^4$ l mol^{-1}mm^{-1} berechnet. Eine Reihe von Alkalimetallsalzen und Metallionen stören nicht. Die Störung durch Nickel(II) wird beseitigt, wenn bei pH 2 extrahiert wird, die durch Eisen(III) durch Maskierung mit EDTA oder durch Reduktion zu Eisen(II). Die Methode ist schnell und genau.

Résumé—On a appliqué avec succès au palladium une méthode d'extraction liquide-liquide du diméthylglyoximate de palladium avec du naphtalène fondu, suivie d'une séparation solide-liquide. Le complexe entre le palladium et la diméthylglyoxime est aisément extrait en naphtalène fondu. Après extraction, les cristaux très fins de naphtalène solidifié sont dissous en chloroforme, et l'on mesure l'absorption de la solution résultante à 370 nm par rapport à un témoin des réactifs. La loi de Beer est suivie pour 30–370 μg de palladium dans 10 ml de chloroforme, et l'on a calculé que le coefficient d'absorption moléculaire est de $1{,}72 \times 10^4$ mm^{-1} l.mole^{-1}. Divers sels alcalins et ions métalliques ne gênent pas. On évite l'interférence du nickel(II) par l'extraction à pH 2, et celle du fer(III) en le dissimulant par l'EDTA ou par réduction en fer(II). La méthode est rapide et précise.

REFERENCES

1. T. Fujinaga, T. Kuwamoto and E. Nakayama, *Talanta*, 1969, **16**, 1225.
2. T. Fujinaga, T. Kuwamoto, T. Yonekubo and M. Satake, *Bunseki Kagaku*, 1969, **18**, 1113.
3. T. Fujinaga, M. Satake and T. Yonekubo, *ibid.*, 1970, **19**, 217.
4. M. Satake, *Memoirs Fac. Engineering, Fukui University*, 1970, **18**, 225.
5. T. Fujinaga, M. Satake and T. Yonekubo, *Bunseki Kagaku*, in the press.

Talanta, 1972, Vol. 19, pp. 692 to 695. Pergamon Press. Printed in Northern Ireland

Détermination gravimétrique de l'iode sous forme de $Nt(ICl_2)$*

(*Reçu le* 28 *avril* 1971. *Accepté le* 28 *novembre* 1971)

ON CONNAÎT deux méthodes de détermination gravimétrique de l'iode. Elles sont basées sur sa précipitation sous forme d'AgI[1] et d'iodure de palladium(II).[2] Une méthode gravimétrique de détermination de l'iode sous forme d'un autre composé, utilisant un agent organique, n'a pas été proposée jusqu'ici. C'est une telle méthode que nous préconisons dans le présent mémoire. L'iode y est déterminé et pesé sous forme de dichloriodure de nitron.

---

* L'abréviation Nt désigne le cation de la base (nitron).

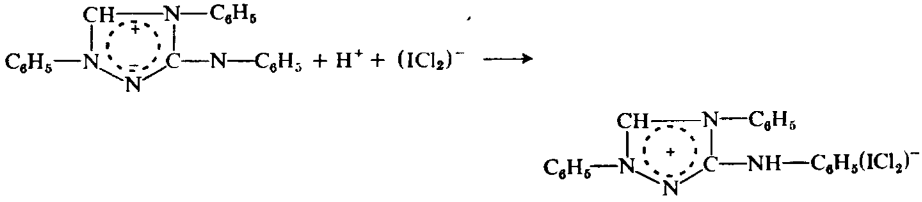
Des essais[3] portant sur le système eau–acide chlorhydrique–iode–chlore, ont montré que lors de son oxydation au moyen du chlore en milieu chlorhydrique saturé de chlore, l'iode se transforme quantitativement en complex $(ICl_2)^-$. On sait que les anions de même type $(ICl_4)^-$ et $(AuCl_4)^-$ réagissant avec certaines bases organique, fournissent des composés peu solubles et que les méthodes de détermination quantitative de la nicotine[4] et de l'or[5] sont basées sur ces propriétés. Ayant en vue ces faits, nous nous sommes proposés pour but d'élaborer une nouvelle méthode gravimétrique de détermination de l'iode, où seraient mises à profit les propriétés du composé que forme le complexe $(ICl_2)^-$ avec le nitron.

PARTIE EXPERIMENTALE

Si l'on additionne une solution contenant le complexe (ICl_2) d'une solution de sulphate de nitron, on obtient un précipité faiblement coloré en jaune qui, après agitation, acquiert une forme nettement cristalline.

Le composé s'obtient en milieu chlorhydrique fortement saturé (d'acide chlorhydrique) offre une solubilité extrêmement faible.

La réaction entre le nitron et le complexe $(ICl_2)^-$ se déroule probablement selon l'équation suivante:



La basicité élevée du nitron provoque la production de protons et l'association du nitron et du complexe iodochlorure. Ce mécanisme se trouve confirmé par les spectres IR du composé obtenu et du nitron. Le spectre du composé, contrairement à celui du nitron, présente un pic de liaison N–H nettement visible.

On a procédé à l'analyse du composé pour en déterminer les teneurs en C, H, N, et la somme de l'iode et du chlore. Les résultats figurent dans le tableau No. I. On y inclu aussi les résultats théoriques, calculés selon les formules: $Nt(ICl_2)$, $Nt(ICl_4)$. Les données du tableau attestent que le composé obtenu est $Nt(ICl_2)$.

TABLEAU I.—DONNÉES SUR LA CONSTITUTION DU COMPOSÉ

	C%	H%	N%	Cl + I%
Théorie pour $Nt(ICl_2)$	47,06	3,34	10,98	38,82
Trouvé	47,4	3,5	10,2	38,6
Théorie pour $Nt(ICl_4)$	43,08	2,95	9,66	46,38

$Nt(ICl_2)$ fond sans se décomposer à 160°C. Il se dissout au mieux dans l'acétone, moins bien dans l'alcool éthylique (0,74%), le dichloréthane (0,40%), le chloroforme (0,06%) et l'éther (0,04%). Il est insoluble dans les solvants non-polaires: benzène, tétrachloromethane. Dans l'eau le composé acquiert une coloration orangée qui, en fin d'opération, vire au noire. Sa solubilité a été déterminée en HCl à 5%, où il ne manifeste pas de modification.

À la température de 20°C, en HCl à 5%, la solubilité est de $6{,}3 \times 10^{-5}M$ en HCl à 5% et en présence de sulfate de nitron que nous avons basé notre nouvelle méthode gravimétrique de détermination de l'iode.

Analyse

Dans un ballon Kjeldahl de 50 ml on introduit environ 20 ml de solution d'ions iodiques contenant de 5 à 40 mg d'iode. On ajoute 20 ml de HCl concentré, saturé en Cl_2, agite, et, aussitôt, on fait barboter de l'air durant 5 minutes à travers cette solution. On transvase le mélange dans une fiole et le dilue à 100 ml, puis on ajoute lentement, et en agitant toujours, 25 ml de solution de sulfate de nitron à 1%. On obtient d'abord un précipité jaune à peine perceptible qui, après agitation énergique, acquiert peu à peu une coloration jaune et une structure cristalline très nette. On laisse reposer pendant une heure, puis on filtre sur un filtre de verre G_3 ou G_4.

Le contenu de la fiole est versé sur le filtre, puis la fiole est rincée par de l'acide chlorhydrique à 4% contenant un peu de sulfate de nitron où, mieux encore, par le filtrat lui-même. Le précipité est ensuite lavé à deux où trois reprises par un peu d'acide chlorhydrique à 4%, sêché pendant 1 hr à 100°–105° et pesé.

Pour illustrer la précision de la méthode, nous avons établi le tableau No. II, qui rend compte des résultats relatifs aux quantités de 4,5 à 40 mg.

Le coefficient de variation pour 15 à 40 mg dans 10 déterminations, evalué pour une sûreté statistique de 95% est respectivement de ±1,70 et ±0,75%.

TABLEAU II.—DETERMINATION DE L'IODE AVEC NITRON

Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %
4,5	4,34	−3,5	15,0	$15,0_6$	+0,4	40,0	$39,8_5$	−0,4
4,5	4,34	−3,5	15,0	$14,9_4$	−0,4	40,0	$39,8_0$	−0,5
4,5	4,39	−2,2	15,0	$14,7_8$	−1,5	40,0	$39,8_0$	−0,5
4,5	4,34	−3,5	15,0	$15,0_8$	+0,5	40,0	$40,0_7$	−0,2
—	—	—	15,0	$15,0_6$	+0,4	40,0	$39,9_7$	−0,1
—	—	—	15,0	$15,0_8$	+0,5	40,0	$39,9_4$	−0,2
—	—	—	15,0	$14,8_8$	−0,8	40,0	$40,2_5$	+0,6
—	—	—	15,0	$15,0_4$	+0,3	40,0	$40,0_0$	±0,0
—	—	—	15,0	$15,0_3$	+0,5	40,0	$39,8_5$	−0,1
—	—	—	15,0	$14,8_1$	−1,3	40,0	$39,8_2$	−0,5
Erreur relat. moyenne		−3,2%			−0,1%			−0,2%

Les ions bromate ne gênent pas la détermination. Si leur quantité est de l'ordre de celle de l'iode, il n'est pas indispensable de changer de mode opératoire. En l'occurence, lors du barbotage, le brome obtenu est éliminé en même temps que l'excédent de chlore, ce qui modifie pas les conditions du travail ultérieur. Si la teneur en Br est élevée, par example si le rapport Br/I = 5–10 et même davantage, la technique doit être modifiée en début d'opération. Dans le ballon de Kjeldahl on doit introduire d'abord de l'acide chlorhydrique concentré et saturé en chlore, puis remplir le ballon de chlore et, alors seulement ajouter à l'aide d'une pipette la solution à analyser. Par la suite, la détermination se déroule selon le schéma décrit plus haut. Dans ces conditions la présence du Br n'a pas d'effet sur les résultats. Ainsi, dans deux déterminations de 40 mg d'I, en présence de la même quantité de Br, on a détecté 40,10 et 40,15 mg d'iode.

La méthode préconisée a été confrontée avec la méthode la plus sûre, pratiquée le plus souvent la détermination gravimétrique de l'iode, sous forme d'AgI. Les résultats de 10 essais de détermination de 15 et de 40 mg d'iode, effectués avec précipitation par l'argent, figurement dans le tableau No. III. La confrontation des données des tableaux II et III, met en évidence d'une façon catégorique la meilleure précision de la nouvelle méthode. Elle présente encore les avantages suivants.

1. Elle se déroule en présence de Cl et de Br.
2. Elle exclu l'erreur due à l'oxydation de I^- en I_2.
3. La décomposition d'AgI, sous l'effet de la lumière n'entraîne pas d'erreurs.
4. Contrairement au précipité d'AgI, celui de $Nt(ICl_2)$ ne retient pas de solvant ni d'autres substances contenues dans la solution.

TABLEAU III.—DETERMINATION DE L'IODE AVEC L'ARGENT

Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %	Prélevé, *mg*	Trouvé, *mg*	Erreur relat., %
15,0	$15,1_6$	+1,1	40,0	40,6	+1,5
15,0	$15,1_6$	+1,1	40,0	40,7	+1,8
15,0	$15,7_1$	+4,7	40,0	40,2	+0,5
15,0	$15,4_3$	+2,8	40,0	39,9	−0,3
15,0	$15,4_8$	+3,2			
15,0	$15,4_3$	+3,0			
Erreur relative moyenne		+2,6%			+0,9%

5. En raison du poids moléculaire élevé et de la faible solubilité de Nt(ICl$_2$), la méthode permet de déterminer des quantités d'iode 2–3 fois plus petites.

6. Pour la même raison, le facteur de transformation du poids du précipité en iode est aussi deux fois plus petit.

7. On utilise le sulfate et non pas l'acétate de nitron, car le nitron, comme reactif, contient beaucoup d'impurités qui, au cours de sa dissolution dans l'acide acétique, restent dans la solution et empêchent la détermination. Au contraire, le sulphate peut être facilement obtenu du nitron.[6]

N. Gantchev
V. Kanazirska
D. Athanassova

Chaire de chimie analytique
Ecole Normale Superieure
7 rue "V. Markov", Plovdiv, Bulgarie

Résumé—On a obtenu le composé dichloriodure de nitron—Nt(ICl$_2$)—et l'on a etudié les propriétés. En se basant sur les résultats obtenus, on a elaboré une méthode gravimétrique de détermination de l'iode sous forme de Nt(ICl$_2$). Elle permet de determiner par voie gravimétrique de 4 à 40 mg d'iode, l'erreur étant moindre que lors de détermination de l'iode sous forme d'AgI. Les ions bromate et chlorate ne gênent pas la détermination.

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

Zusammenfassung—Nitrondichlorojodid—Nt(JCl$_2$)—wurde hergestellt und untersucht; auf den Ergebnissen wurde eine gravimetrische Bestimmung von Jod als Nt(JCl$_2$) aufgebaut. Für 4–40 mg Jod ist der Fehler kleiner als bei der Bestimmung als AgJ. Bromat und Chlorat stören nicht.

BIBLIOGRAPHIE

1. W. F. Hillebrand, G. E. F. Lundell, H. I. Bright et J. A. Hoffman, *Applied Inorganic Analysis*, (*Russian Edition*), p. 816, 1966.
2. R. Streibinger et J. Pollak, *Microchemie*, 1925, **3**, 38.
3. N. Gantchev et D. Athanassova, *Trav. Sci.*, *Ecole Normale Superieure*, *Plovdiv* 1972, 2.
4. F. D. Chattaway et G. D. Parkes, *J. Chem. Soc.*, 1929, 1314.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Ukr. Akad. Nauk.*, 1970, **36**, 1184.
6. A. S. Babenko, V. N. Tolmatchev et A. N. Didzin, *Ukr. Khim. Zh.*, 1963, **29**, 702.

Talanta, 1972, Vol. 19, pp. 695 to 697. Pergamon Press. Printed in Northern Ireland

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten

(*Eingegangen am* 19. *Juli* 1971. *Angenommen am* 18. *Oktober* 1971)

Die analytische Chemie der Phosphate gewinnt auf Grund der vielfältigen Formen und des häufigen Auftretens dieser Verbindungen in Natur- und Syntheseprodukten zunehmend an Bedeutung. Bisherige papierchromatographische[1,2] und dünnschicht-chromatographische Trennungen (an Celluloseschichten)[3] zeigen zwar gute Ergebnisse, sind aber nur schwer reproduzierbar. Im Gegensatz dazu liefert die Gradientenelution an Anionenaustauscher-Säulen[4,5] sehr gute Ergebnisse, jedoch ist dieses Verfahren sehr zeitaufwendig. Um die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches zu verbinden, wendeten wir die Ionenaustauscher-Dünnschichtchromatographie an.[6,7] Wir verwendeten selbst gefertigte Anionenaustauscher-Fertigplatten (200 × 200 mm) vom Typ Dowex 2-X8, die sowohl in der Chlorid-, als auch in der Acetat-Form vorlagen. Zum Vergleich wurden auch einige "Ionex 25" Anionenaustauscher-Fertigplatten des gleichen Typs der Firma Macherey-Nagel (Düren, BRD) in der Acetat-Form herangezogen.

5. En raison du poids moléculaire élevé et de la faible solubilité de Nt(ICl$_2$), la méthode permet de déterminer des quantités d'iode 2–3 fois plus petites.

6. Pour la même raison, le facteur de transformation du poids du précipité en iode est aussi deux fois plus petit.

7. On utilise le sulfate et non pas l'acétate de nitron, car le nitron, comme reactif, contient beaucoup d'impurités qui, au cours de sa dissolution dans l'acide acétique, restent dans la solution et empêchent la détermination. Au contraire, le sulphate peut être facilement obtenu du nitron.[6]

N. Gantchev
V. Kanazirska
D. Athanassova

Chaire de chimie analytique
Ecole Normale Superieure
7 rue "V. Markov", Plovdiv, Bulgarie

Résumé—On a obtenu le composé dichloriodure de nitron—Nt(ICl$_2$)—et l'on a etudié les propriétés. En se basant sur les résultats obtenus, on a elaboré une méthode gravimétrique de détermination de l'iode sous forme de Nt(ICl$_2$). Elle permet de determiner par voie gravimétrique de 4 à 40 mg d'iode, l'erreur étant moindre que lors de détermination de l'iode sous forme d'AgI. Les ions bromate et chlorate ne gênent pas la détermination.

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

Zusammenfassung—Nitrondichlorojodid—Nt(JCl$_2$)—wurde hergestellt und untersucht; auf den Ergebnissen wurde eine gravimetrische Bestimmung von Jod als Nt(JCl$_2$) aufgebaut. Für 4–40 mg Jod ist der Fehler kleiner als bei der Bestimmung als AgJ. Bromat und Chlorat stören nicht.

BIBLIOGRAPHIE

1. W. F. Hillebrand, G. E. F. Lundell, H. I. Bright et J. A. Hoffman, *Applied Inorganic Analysis*, (*Russian Edition*), p. 816, 1966.
2. R. Streibinger et J. Pollak, *Microchemie*, 1925, 3, 38.
3. N. Gantchev et D. Athanassova, *Trav. Sci.*, *Ecole Normale Superieure*, *Plovdiv* 1972, 2.
4. F. D. Chattaway et G. D. Parkes, *J. Chem. Soc.*, 1929, 1314.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Ukr. Akad. Nauk.*, 1970, 36, 1184.
6. A. S. Babenko, V. N. Tolmatchev et A. N. Didzin, *Ukr. Khim. Zh.*, 1963, 29, 702.

Talanta, 1972, Vol. 19, pp. 695 to 697. Pergamon Press. Printed in Northern Ireland

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten

(*Eingegangen am* 19. *Juli* 1971. *Angenommen am* 18. *Oktober* 1971)

Die analytische Chemie der Phosphate gewinnt auf Grund der vielfältigen Formen und des häufigen Auftretens dieser Verbindungen in Natur- und Syntheseprodukten zunehmend an Bedeutung. Bisherige papierchromatographische[1,2] und dünnschicht-chromatographische Trennungen (an Celluloseschichten)[3] zeigen zwar gute Ergebnisse, sind aber nur schwer reproduzierbar. Im Gegensatz dazu liefert die Gradientenelution an Anionenaustauscher-Säulen[4,5] sehr gute Ergebnisse, jedoch ist dieses Verfahren sehr zeitaufwendig. Um die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches zu verbinden, wendeten wir die Ionenaustauscher-Dünnschichtchromatographie an.[6,7] Wir verwendeten selbst gefertigte Anionenaustauscher-Fertigplatten (200 × 200 mm) vom Typ Dowex 2-X8, die sowohl in der Chlorid-, als auch in der Acetat-Form vorlagen. Zum Vergleich wurden auch einige "Ionex 25" Anionenaustauscher-Fertigplatten des gleichen Typs der Firma Macherey-Nagel (Düren, BRD) in der Acetat-Form herangezogen.

EXPERIMENTELLER TEIL

Pufferlösung: pH = 5,0. Die Lösung enthält pro Liter 20 ml Pyridin und 13,4 ml Eisessig. Zur Trennung der Oligophosphate werden zu dieser Stamm-Pufferlösung noch 0,25 Mol Natrium chlorid zugesetzt.

Bedingungen. Es wurden ungefähr 1 μg P von jeder Phosphor(v)-Verbindung auf die Platte aufgetragen. Zur Trennung der Oligophosphate äquilibrierten wir die Schicht mit $1M$ Salzsäure durch durchlaufende Chromatographie mit Papierzunge. Nach einem kurzen Zwischentrocknen wuschen wir die Platten mit ionenfreiem Wasser säurefrei. Zur Trennung der Amidophosphate erfolgte die Äquilibrierung nach der gleichen Methode jedoch ohne Nachwaschen mit $0{,}01M$ Essigsäure. Die Trennung der Oligophosphate geschah bei Zimmertemperatur, die der Amidophosphate bei etwa 5° im Kühlschrank. Bei beiden wurde die aufsteigende Technik angewendet. Die Laufzeit betrug in beiden Fällen ungefähr 70 Minuten.

Sprühreagenzien

(*a*) $1M$ Perchlorsäure, in Wasser–Aceton 1:1. Zur Hydrolyse von Di- und Triphosphat zu Monophosphat wird diese Lösung zweimal auf die warme Platte 60° aufgesprüht. Nach dem zweiten Besprühen wird die Platte langsam bei 50° getrocknet. Bei den Amidophosphaten erübrigt sich dieser Aufschluß.

(*b*) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(5 g) wird in einer Mischung aus 35 ml halbkonzentrierter Salpetersäure und 65 ml Wasser aufgelöst. Mit dieser Lösung wird die noch warme Platte befeuchtet.

(*c*) $SnCl_2\cdot 2H_2O$(0,5 g) wird in 100 ml $0{,}5M$ Salzsäure gelöst. Die Lösung wird auf die noch feuchte Platte gesprüht. Die Phosphate treten als blaue bis blau-grüne Flecke hervor.

Mono-, Di- und Triphosphat werden an einer Fertigplatte in der Chlorid-Form einwandfrei getrennt. Wie nicht anders zu erwarten, befindet sich das Triphosphat auf Grund seiner großen Ladung nur kurz oberhalb des Startpunktes. Diphosphat und Monophosphat wandern wegen der abnehmenden Ladungszahl entsprechend weiter.

Zur Trennung von Phosphorsäuretriamid, $PO(NH_2)_3$, Diamidophosphat, $NaPO_2(NH_2)_2$, Monoamidophosphat, $Na_2PO_3(NH_2)$ und Monophosphat, Na_2HPO_4, empfiehlt sich die Anwendung eines schwächeren Gegenions am Anionenaustauscher. Da erfahrungsgemäß die Amidophosphate auf den Chromatogrammen vor dem Monophosphat liegen, würden sie auf einer Anionenaustauscher-Fertigplatte in der Chlorid-Form nur kurz unterhalb der Front liegen und sich gegenseitig stören. Um eine Zersetzung der Amidophosphate so weit wie möglich zu verhindern, wurde die Entwicklung bei der angegebenen niedrigen Temperatur durchgeführt.

Die von uns vorgeschlagen Methode besitzt neben dem geringen Zeitaufwand und der großen Reproduzierbarkeit der Ergebnisse noch folgende Vorteile: die Trennung der Oligophosphate und der Amidophosphate kann im Prinzip mit nur einer Stamm-Pufferlösung vorgenommen werden. Bei der Trennung der Oligophosphate stören die Amidophosphate nicht, da sie vor dem Monophosphat liegen. Im umgekehrten Fall verbleiben die Oligophosphate am Start. Ein Vergleich mit den Ionenaustauscher-Fertigplatten "Ionex 25" ergab, daß keine bedeutenden Unterschiede in den Trennungen auftreten.

Anmerkung—An dieser Stelle möchte einer der Verfasser, H. K., Herrn Dr. T. Dévényi für die Überlassung der Anionenaustauscher Fertigplatten und für seine anregenden Diskussionen herzlich danken.

Institut für Allgemeine und Analytische Chemie H. KROSCHWITZ
Technische Universität E. PUNGOR
Budapest XI
Gellért tér 4
Hungary

Institut für Biochemie der Ungarischen Akademie der Wissenschaften S. FERENCZI
Budapest XI
Karolina út 29–31

Zusammenfassung—Es wird ein Verfahren zur Trennung von Monophosphat, Diphosphat und Triphosphat bzw. Phosphorsäuretriamid, $PO(NH_2)_3$, Diamidophosphat, $NaPO_2(NH_2)_2$, Monoamidophosphat, $Na_2PO_3NH_2$ und Monophosphat an Anionenaustauscher-Fertigplatten des Typs Dowex 2-X8 beschrieben. Das Verfahren verbindet die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches. Durch die Auswahl geeigneter Gegenionen am Harz (Chlorid bzw.

Acetat) ist im Prinzip nur eine Stamm-Pufferlösung zur Trennung erforderlich. Bei der Chromatographie tritt keine Störung beider Verbindungsklassen auf.

Summary—A procedure is described for the separation of mono-, di- and triphosphate, and of monophosphate and mono, di- and triamidophosphate on ready-made thin-layer plates of anion-exchange resin Dowex 2-X8. The procedure couples the advantages of thin-layer chromatography with those of ion-exchange techniques. By suitable choice of anion for the resin (*i.e.* chloride or acetate) only one stock buffer solution is needed for the separation. The two classes of compounds do not interfere with each other during the separations.

Résumé—On décrit une technique pour la séparation de mono-, di- et triphosphate, et de monophosphate et mono-, di- et triamidophosphate sur des plaques de couche mince de résine échangeuse d'anions Dowex 2-X8 toutes prêtes. La méthode réunit les avantages de la chromatographie sur couche mince avec ceux des techniques d'échange d'ions. Par un choix convenable de l'anion pour la résine (c'est-à-dire chlorure ou acétate), une seule solution tampon de réserve est nécessaire pour la séparation. Les deux classes de composés n'interfèrent pas l'une avec l'autre durant les séparations.

LITERATUR

1. E. H. G. Thilo, *Die Papierchromatographie der kondensierten Phosphate*. Akademie Verlag Berlin, 1955.
2. G. Z. Biberacher, *Z. Anorg. Allgem. Chem.*, 1956, **285**, 88.
3. E. F. Wagner, *Seifen Öle Fette Wachse*, 1967, **93**, 865.
4. J. Inczédy, *Analytische Anwendungen von Ionenaustauschern*. Akadémiai Kiadó, Budapest, 1964.
5. J. A. Grande und J. Beukenkamp, *Anal. Chem.*, 1956, **28**, 1497.
6. T. Dévényi und S. Zoltán, *7th Intern. Symp. Chem. Natural Products*, Riga, 1970, S. 52.
7. S. Ferenczi und T. Dévényi, *Acta Biochim. Biophys. Acad. Sci. Hung.* (im Druck).

5. En raison du poids moléculaire élevé et de la faible solubilité de Nt(ICl$_2$), la méthode permet de déterminer des quantités d'iode 2–3 fois plus petites.

6. Pour la même raison, le facteur de transformation du poids du précipité en iode est aussi deux fois plus petit.

7. On utilise le sulfate et non pas l'acétate de nitron, car le nitron, comme reactif, contient beaucoup d'impurités qui, au cours de sa dissolution dans l'acide acétique, restent dans la solution et empêchent la détermination. Au contraire, le sulphate peut être facilement obtenu du nitron.[6]

N. Gantchev
V. Kanazirska
D. Athanassova

Chaire de chimie analytique
Ecole Normale Superieure
7 rue "V. Markov", Plovdiv, Bulgarie

Résumé—On a obtenu le composé dichloriodure de nitron—Nt(ICl$_2$)—et l'on a etudié les propriétés. En se basant sur les résultats obtenus, on a elaboré une méthode gravimétrique de détermination de l'iode sous forme de Nt(ICl$_2$). Elle permet de determiner par voie gravimétrique de 4 à 40 mg d'iode, l'erreur étant moindre que lors de détermination de l'iode sous forme d'AgI. Les ions bromate et chlorate ne gênent pas la détermination.

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

Zusammenfassung—Nitrondichlorojodid—Nt(JCl$_2$)—wurde hergestellt und untersucht; auf den Ergebnissen wurde eine gravimetrische Bestimmung von Jod als Nt(JCl$_2$) aufgebaut. Für 4–40 mg Jod ist der Fehler kleiner als bei der Bestimmung als AgJ. Bromat und Chlorat stören nicht.

BIBLIOGRAPHIE

1. W. F. Hillebrand, G. E. F. Lundell, H. I. Bright et J. A. Hoffman, *Applied Inorganic Analysis*, (*Russian Edition*), p. 816, 1966.
2. R. Streibinger et J. Pollak, *Microchemie*, 1925, 3, 38.
3. N. Gantchev et D. Athanassova, *Trav. Sci.*, *Ecole Normale Superieure*, *Plovdiv* 1972, 2.
4. F. D. Chattaway et G. D. Parkes, *J. Chem. Soc.*, 1929, 1314.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Ukr. Akad. Nauk.*, 1970, **36**, 1184.
6. A. S. Babenko, V. N. Tolmatchev et A. N. Didzin, *Ukr. Khim. Zh.*, 1963, **29**, 702.

Talanta, 1972, Vol. 19, pp. 695 to 697. Pergamon Press. Printed in Northern Ireland

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten

(*Eingegangen am* 19. *Juli* 1971. *Angenommen am* 18. *Oktober* 1971)

Die analytische Chemie der Phosphate gewinnt auf Grund der vielfältigen Formen und des häufigen Auftretens dieser Verbindungen in Natur- und Syntheseprodukten zunehmend an Bedeutung. Bisherige papierchromatographische[1,2] und dünnschicht-chromatographische Trennungen (an Celluloseschichten)[3] zeigen zwar gute Ergebnisse, sind aber nur schwer reproduzierbar. Im Gegensatz dazu liefert die Gradientenelution an Anionenaustauscher-Säulen[4,5] sehr gute Ergebnisse, jedoch ist dieses Verfahren sehr zeitaufwendig. Um die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches zu verbinden, wendeten wir die Ionenaustauscher-Dünnschichtchromatographie an.[6,7] Wir verwendeten selbst gefertigte Anionenaustauscher-Fertigplatten (200 × 200 mm) vom Typ Dowex 2-X8, die sowohl in der Chlorid-, als auch in der Acetat-Form vorlagen. Zum Vergleich wurden auch einige "Ionex 25" Anionenaustauscher-Fertigplatten des gleichen Typs der Firma Macherey-Nagel (Düren, BRD) in der Acetat-Form herangezogen.

EXPERIMENTELLER TEIL

Pufferlösung: pH = 5,0. Die Lösung enthält pro Liter 20 ml Pyridin und 13,4 ml Eisessig. Zur Trennung der Oligophosphate werden zu dieser Stamm-Pufferlösung noch 0,25 Mol Natrium chlorid zugesetzt.

Bedingungen. Es wurden ungefähr 1 μg P von jeder Phosphor(v)-Verbindung auf die Platte aufgetragen. Zur Trennung der Oligophosphate äquilibrierten wir die Schicht mit 1*M* Salzsäure durch durchlaufende Chromatographie mit Papierzunge. Nach einem kurzen Zwischentrocknen wuschen wir die Platten mit ionenfreiem Wasser säurefrei. Zur Trennung der Amidophosphate erfolgte die Äquilibrierung nach der gleichen Methode jedoch ohne Nachwaschen mit 0,01*M* Essigsäure. Die Trennung der Oligophosphate geschah bei Zimmertemperatur, die der Amidophosphate bei etwa 5° im Kühlschrank. Bei beiden wurde die aufsteigende Technik angewendet. Die Laufzeit betrug in beiden Fällen ungefähr 70 Minuten.

Sprühreagenzien

(*a*) 1*M* Perchlorsäure, in Wasser–Aceton 1:1. Zur Hydrolyse von Di- und Triphosphat zu Monophosphat wird diese Lösung zweimal auf die warme Platte 60° aufgesprüht. Nach dem zweiten Besprühen wird die Platte langsam bei 50° getrocknet. Bei den Amidophosphaten erübrigt sich dieser Aufschluß.

(*b*) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(5 g) wird in einer Mischung aus 35 ml halbkonzentrierter Salpetersäure und 65 ml Wasser aufgelöst. Mit dieser Lösung wird die noch warme Platte befeuchtet.

(*c*) $SnCl_2\cdot 2H_2O$(0,5 g) wird in 100 ml 0,5*M* Salzsäure gelöst. Die Lösung wird auf die noch feuchte Platte gesprüht. Die Phosphate treten als blaue bis blau-grüne Flecke hervor.

Mono-, Di- und Triphosphat werden an einer Fertigplatte in der Chlorid-Form einwandfrei getrennt. Wie nicht anders zu erwarten, befindet sich das Triphosphat auf Grund seiner großen Ladung nur kurz oberhalb des Startpunktes. Diphosphat und Monophosphat wandern wegen der abnehmenden Ladungszahl entsprechend weiter.

Zur Trennung von Phosphorsäuretriamid, $PO(NH_2)_3$, Diamidophosphat, $NaPO_2(NH_2)_2$, Monoamidophosphat, $Na_2PO_3(NH_2)$ und Monophosphat, Na_2HPO_4, empfiehlt sich die Anwendung eines schwächeren Gegenions am Anionenaustauscher. Da erfahrungsgemäß die Amidophosphate auf den Chromatogrammen vor dem Monophosphat liegen, würden sie auf einer Anionenaustauscher-Fertigplatte in der Chlorid-Form nur kurz unterhalb der Front liegen und sich gegenseitig stören. Um eine Zersetzung der Amidophosphate so weit wie möglich zu verhindern, wurde die Entwicklung bei der angegebenen niedrigen Temperatur durchgeführt.

Die von uns vorgeschlagen Methode besitzt neben dem geringen Zeitaufwand und der großen Reproduzierbarkeit der Ergebnisse noch folgende Vorteile: die Trennung der Oligophosphate und der Amidophosphate kann im Prinzip mit nur einer Stamm-Pufferlösung vorgenommen werden. Bei der Trennung der Oligophosphate stören die Amidophosphate nicht, da sie vor dem Monophosphat liegen. Im umgekehrten Fall verbleiben die Oligophosphate am Start. Ein Vergleich mit den Ionenaustauscher-Fertigplatten "Ionex 25" ergab, daß keine bedeutenden Unterschiede in den Trennungen auftreten.

Anmerkung—An dieser Stelle möchte einer der Verfasser, H. K., Herrn Dr. T. Dévényi für die Uberlassung der Anionenaustauscher Fertigplatten und für seine anregenden Diskussionen herzlich danken.

Institut für Allgemeine und Analytische Chemie H. Kroschwitz
Technische Universität E. Pungor
Budapest XI
Gellért tér 4
Hungary

Institut für Biochemie der Ungarischen Akademie der Wissenschaften S. Ferenczi
Budapest XI
Karolina út 29–31

Zusammenfassung—Es wird ein Verfahren zur Trennung von Monophosphat, Diphosphat und Triphosphat bzw. Phosphorsäuretriamid, $PO(NH_2)_3$, Diamidophosphat, $NaPO_2(NH_2)_2$, Monoamidophosphat, $Na_2PO_3NH_2$ und Monophosphat an Anionenaustauscher-Fertigplatten des Typs Dowex 2-X8 beschrieben. Das Verfahren verbindet die Vorteile der Dünnschichtchromatographie mit denen des Ionenaustausches. Durch die Auswahl geeigneter Gegenionen am Harz (Chlorid bzw.

Acetat) ist im Prinzip nur eine Stamm-Pufferlösung zur Trennung erforderlich. Bei der Chromatographie tritt keine Störung beider Verbindungsklassen auf.

Summary—A procedure is described for the separation of mono-, di- and triphosphate, and of monophosphate and mono, di- and triamidophosphate on ready-made thin-layer plates of anion-exchange resin Dowex 2-X8. The procedure couples the advantages of thin-layer chromatography with those of ion-exchange techniques. By suitable choice of anion for the resin (*i.e.* chloride or acetate) only one stock buffer solution is needed for the separation. The two classes of compounds do not interfere with each other during the separations.

Résumé—On décrit une technique pour la séparation de mono-, di- et triphosphate, et de monophosphate et mono-, di- et triamidophosphate sur des plaques de couche mince de résine échangeuse d'anions Dowex 2-X8 toutes prêtes. La méthode réunit les avantages de la chromatographie sur couche mince avec ceux des techniques d'échange d'ions. Par un choix convenable de l'anion pour la résine (c'est-à-dire chlorure ou acétate), une seule solution tampon de réserve est nécessaire pour la séparation. Les deux classes de composés n'interfèrent pas l'une avec l'autre durant les séparations.

LITERATUR

1. E. H. G. Thilo, *Die Papierchromatographie der kondensierten Phosphate.* Akademie Verlag Berlin, 1955.
2. G. Z. Biberacher, *Z. Anorg. Allgem. Chem.*, 1956, **285**, 88.
3. E. F. Wagner, *Seifen Öle Fette Wachse*, 1967, **93**, 865.
4. J. Inczédy, *Analytische Anwendungen von Ionenaustauschern.* Akadémiai Kiadó, Budapest, 1964.
5. J. A. Grande und J. Beukenkamp, *Anal. Chem.*, 1956, **28**, 1497.
6. T. Dévényi und S. Zoltán, *7th Intern. Symp. Chem. Natural Products*, Riga, 1970, S. 52.
7. S. Ferenczi und T. Dévényi, *Acta Biochim. Biophys. Acad. Sci. Hung.* (im Druck).

Talanta, 1972, Vol. 19, pp. 699 to 700. Pergamon Press. Printed in Northern Ireland

ANALYTICAL DATA

Potentiometric determination of stepwise stability constants of zirconium and thorium chelates formed with aspartic and glutamic acids

(*Received* 29 *September* 1971. *Accepted* 18 *October* 1971)

ASPARTIC and glutamic acids are known to form chelate complexes with various metal ions,[1–7] in which they act as bidentate or tridentate ligands. In previous communications[8,9] from this laboratory we reported stepwise stability constants of aspartate and glutamate chelates of Hg(II), Be(II), Al(III), Pd(II), Pt(IV), Au(III) and Bi(III). Their formation was studied potentiometrically by Calvin-Bjerrum's pH titration technique[10] as modified by Irving and Rossotti.[11] This paper gives the results of a similar study with zirconium(IV) and thorium(IV) ions.

RESULTS AND DISCUSSION

The protonation constants are log K_1^{H} 9·48, log K_2^{H} 3·75 for aspartic acid, and log K_1^{H} 9·45 and og K_2^{H} 4·23 for glutamic acid.[8,9]

The formation curves ($\bar{n}$ *vs.* pL) for the aspartate and glutamate chelates show that for Zr(IV) $\bar{n}$ approaches a value of 3, whereas for Th(IV) $\bar{n}$ approaches a maximum value of 4 (pH range 3-9).

Analysis of the formation curves for the Zr(IV) chelates shows that K_1, K_2, K_3 are well apart, with $K_1/K_2 \sim 10^3$ K_2/K_3 ratio $\sim 10^3$. The stability constants were computed by interpolation at half-$\bar{n}$ values[11] and also by successive approximation method.

For Th(IV) chelates, however, $K_1/K_2 \sim 10^{0.8}$ $K_2/K_3 \sim 10^4$ and $K_3/K_4 \sim 10^{0.8}$, so the formation curves can be divided into two separate regions, and each treated separately.[12] In the range $\bar{n} = 0$–2 approximate constants were obtained by interpolation at half-$\bar{n}$ values, and then refined by successive approximation. The results are further confirmed by the correction term method. In the second range ($\bar{n} = 2$–4) also, K_3 and K_4 were computed by the half-$\bar{n}$ and the correction term methods. The constants were further refined by successive approximation.

TABLE I.—STABILITY CONSTANTS OF ZIRCONIUM(IV) AND THORIUM(IV) CHELATES WITH ASPARTIC AND GLUTAMIC ACIDS.
(Temp. 25°C, $\mu = 0{\cdot}1M$ NaClO$_4$)

Metal ion	Method	Aspartic acid				Glutamic acid			
		log K_1	log K_2	log K_3	log β_3	log K_1	log K_2	log K_3	log β_3
Zr(IV)	Half $\bar{n}$ method	9·70	6·85	3·50	20·05	9·60	6·40	3·32	19·32
	Successive approximation method	9·70	6·85	3·50	20·05	9·60	6·40	3·32	19·32

Metal ion	Method	log K_1	log K_2	log K_3	log K_4	log β_4	log K_1	log K_2	log K_3	log K_4	log β_4
Th(IV)	Interpolation at half $\bar{n}$ values	9·38	8·55	4·70	3·87	—	9·25	8·50	4·27	3·60	—
	Correction term method	9·10	8·78	4·56	4·07	26·51	9·09	8·52	4·20	3·73	25·54
	Successive approximation method	9·23	8·57	4·55	3·87	26·22	9·11	8·52	4·18	3·62	25·43

Chemical Laboratories
University of Allahabad
Allahabad (India)

M. K. SINGH
M. N. SRIVASTAVA*

---

* Postal address: 266, Mumfordganj Near Distillery, Allahabad, India.

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in 0·1*M* sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Zusammenfassung—Die Metallchelate von Zr(IV) und Th(IV) mit Asparaginsäure und Glutaminsäure wurden potentiometrisch untersucht. Die Bildungskonstanten der einzelnen Stufen in 0,1*M* Natriumperchlorat bei 25° werden mitgeteilt: Asparaginsäure-Chelate—log K_1 9,70, log K_2 6,85, log K_3 3,50 für Zr und log K_1 9,23, log K_2 8,57, log K_3 4,55, log K_4 3,87 für Th; Glutaminsäure-Chelate—log K_1 9,60, log K_2 6,40, log K_3 3,32 für Zr und log K_1 9,11, log K_2 8,52, log K_3 4,18, log K_4 3,62 für Th.

Résumé—Les chèlates mètalliques de Zr(IV) et Th(IV) avec les acides aspartique et glutamique ont ètè ètudiès potentiomètriquement. Les constantes de stabilitè par palier en perchlorate de sodium 0,1 *M* à 25° sont: chèlates aspartiques—log K_1 9,70; log K_2 6,85; et log K_3 3,50 pour Zr et log K_1 9,23; log K$_2$ 8,57, log K_3 4,55 et log K_4 3,87 pour Th; chèlates glutamiques—log K_1 9,60, log K_2 6,40 et log K_3 3,32 pour Zr et log K_1 9,11; log K$_2$ 8,52; log K$_3$ 4,18 et log K_4 3,62 pour Th.

REFERENCES

1. S. Chaberek, Jr. and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 6021.
2. N. C. Li and E. Doody, *ibid.*, 1952, **74**, 4184.
3. R. E. Lumb and A. E. Martell, *J. Phys. Chem.*, 1953, **57**, 690.
4. M. Batyaev, S. V. Larionov and V. M. Shul'man, *Zh. Neorgan. Khim.*, 1961, **6**, 153.
5. M. Cefola, A. S. Tompa, A. V. Celiano and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290.
6. E. E. Kriss, *Ukr. Khim. Zh.*, 1964 **31**, 328.
7. H. Mizuochi, S. Shirakata, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1970, **43**, 397.
8. M. K. Singh and M. N. Srivastava, *Vij. Pari. Anu. Patrika*, in the press.
9. *Idem*, *J. Inorg. Nucl. Chem.*, in the press.
10. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
11. H. Irving and H. S. Rossotti, *J, Chem. Soc.*, 1953, 3397; 1954, 2904.
12. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 106. McGraw-Hill, New York, 1961.

Talanta, 1972, Vol. 19, pp. 700 to 706. Pergamon Press. Printed in Northern Ireland

Thermodynamic dissociation constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid

(*Received* 23 *June* 1971. *Accepted* 17 *November* 1971)

THE p*K* VALUES of benzohydroxamic acid and substituted phenylbenzohydroxamic acids have been determined in 10–50% v/v dioxan-water media at 25° and 30°. The van Uitert and Haas relation[1] was used to obtain the hydrogen ion concentration from the values read on the pH-meter:

$$-\log [\mathrm{H}^+] = \mathrm{pH} + \log U_{\mathrm{H}}{}^0 - \log \frac{1}{\gamma_\pm}$$

Talanta, 1972, Vol. 19, pp. 699 to 700. Pergamon Press. Printed in Northern Ireland

ANALYTICAL DATA

Potentiometric determination of stepwise stability constants of zirconium and thorium chelates formed with aspartic and glutamic acids

(*Received* 29 *September* 1971. *Accepted* 18 *October* 1971)

ASPARTIC and glutamic acids are known to form chelate complexes with various metal ions,[1–7] in which they act as bidentate or tridentate ligands. In previous communications[8,9] from this laboratory we reported stepwise stability constants of aspartate and glutamate chelates of Hg(II), Be(II), Al(III), Pd(II), Pt(IV), Au(III) and Bi(III). Their formation was studied potentiometrically by Calvin-Bjerrum's pH titration technique[10] as modified by Irving and Rossotti.[11] This paper gives the results of a similar study with zirconium(IV) and thorium(IV) ions.

RESULTS AND DISCUSSION

The protonation constants are log K_1^H 9·48, log K_2^H 3·75 for aspartic acid, and log K_1^H 9·45 and og K_2^H 4·23 for glutamic acid.[8,9]

The formation curves ($\bar{n}$ *vs.* pL) for the aspartate and glutamate chelates show that for Zr(IV) $\bar{n}$ approaches a value of 3, whereas for Th(IV) $\bar{n}$ approaches a maximum value of 4 (pH range 3-9).

Analysis of the formation curves for the Zr(IV) chelates shows that K_1, K_2, K_3 are well apart, with $K_1/K_2 \sim 10^3$ K_2/K_3 ratio $\sim 10^3$. The stability constants were computed by interpolation at half-$\bar{n}$ values[11] and also by successive approximation method.

For Th(IV) chelates, however, $K_1/K_2 \sim 10^{0 \cdot 8}$ $K_2/K_3 \sim 10^4$ and $K_3/K_4 \sim 10^{0 \cdot 8}$, so the formation curves can be divided into two separate regions, and each treated separately.[12] In the range $\bar{n} = 0$–2 approximate constants were obtained by interpolation at half-$\bar{n}$ values, and then refined by successive approximation. The results are further confirmed by the correction term method. In the second range ($\bar{n} = 2$–4) also, K_3 and K_4 were computed by the half-$\bar{n}$ and the correction term methods. The constants were further refined by successive approximation.

TABLE I.—STABILITY CONSTANTS OF ZIRCONIUM(IV) AND THORIUM(IV) CHELATES WITH ASPARTIC AND GLUTAMIC ACIDS.
(Temp. 25°C, $\mu = 0 \cdot 1 M$ NaClO$_4$)

Metal ion	Method	Aspartic acid				Glutamic acid			
		log K_1	log K_2	log K_3	log β_3	log K_1	log K_2	log K_3	log β_3
Zr(IV)	Half $\bar{n}$ method	9·70	6·85	3·50	20·05	9·60	6·40	3·32	19·32
	Successive approximation method	9·70	6·85	3·50	20·05	9·60	6·40	3·32	19·32

Metal ion	Method	log K_1	log K_2	log K_3	log K_4	log β_4	log K_1	log K_2	log K_3	log K_4	log β_4
Th(IV)	Interpolation at half $\bar{n}$ values	9·38	8·55	4·70	3·87	—	9·25	8·50	4·27	3·60	—
	Correction term method	9·10	8·78	4·56	4·07	26·51	9·09	8·52	4·20	3·73	25·54
	Successive approximation method	9·23	8·57	4·55	3·87	26·22	9·11	8·52	4·18	3·62	25·43

Chemical Laboratories
University of Allahabad
Allahabad (India)

M. K. SINGH
M. N. SRIVASTAVA*

---

* Postal address: 266, Mumfordganj Near Distillery, Allahabad, India.

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in 0·1*M* sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Zusammenfassung—Die Metallchelate von Zr(IV) und Th(IV) mit Asparaginsäure und Glutaminsäure wurden potentiometrisch untersucht. Die Bildungskonstanten der einzelnen Stufen in 0,1*M* Natriumperchlorat bei 25° werden mitgeteilt: Asparaginsäure-Chelate—log K_1 9,70, log K_2 6,85, log K_3 3,50 für Zr und log K_1 9,23, log K_2 8,57, log K_3 4,55, log K_4 3,87 für Th; Glutaminsäure-Chelate—log K_1 9,60, log K_2 6,40, log K_3 3,32 für Zr und log K_1 9,11, log K_2 8,52, log K_3 4,18, log K_4 3,62 für Th.

Résumé—Les chèlates mètalliques de Zr(IV) et Th(IV) avec les acides aspartique et glutamique ont ètè ètudiès potentiomètriquement. Les constantes de stabilitè par palier en perchlorate de sodium 0,1 *M* à 25° sont: chèlates aspartiques—log K_1 9,70; log K_2 6,85; et log K_3 3,50 pour Zr et log K_1 9,23; log K_2 8,57, log K_3 4,55 et log K_4 3,87 pour Th; chèlates glutamiques—log K_1 9,60, log K_2 6,40 et log K_3 3,32 pour Zr et log K_1 9,11; log K_2 8,52; log K_3 4,18 et log K_4 3,62 pour Th.

REFERENCES

1. S. Chaberek, Jr. and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 6021.
2. N. C. Li and E. Doody, *ibid.*, 1952, **74**, 4184.
3. R. E. Lumb and A. E. Martell, *J. Phys. Chem.*, 1953, **57**, 690.
4. M. Batyaev, S. V. Larionov and V. M. Shul'man, *Zh. Neorgan. Khim.*, 1961, **6**, 153.
5. M. Cefola, A. S. Tompa, A. V. Celiano and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290.
6. E. E. Kriss, *Ukr. Khim. Zh.*, 1964 **31**, 328.
7. H. Mizuochi, S. Shirakata, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1970, **43**, 397.
8. M. K. Singh and M. N. Srivastava, *Vij. Pari. Anu. Patrika*, in the press.
9. *Idem*, *J. Inorg. Nucl. Chem.*, in the press.
10. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
11. H. Irving and H. S. Rossotti, *J, Chem. Soc.*, 1953, 3397; 1954, 2904.
12. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 106. McGraw-Hill, New York, 1961.

Talanta, 1972, Vol. 19, pp. 700 to 706. Pergamon Press. Printed in Northern Ireland

Thermodynamic dissociation constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid

(*Received* 23 *June* 1971. *Accepted* 17 *November* 1971)

THE p*K* VALUES of benzohydroxamic acid and substituted phenylbenzohydroxamic acids have been determined in 10–50% v/v dioxan–water media at 25° and 30°. The van Uitert and Haas relation[1] was used to obtain the hydrogen ion concentration from the values read on the pH-meter:

$$-\log [\mathrm{H}^+] = \mathrm{pH} + \log U_{\mathrm{H}}{}^0 - \log \frac{1}{\gamma_{\pm}}$$

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in $0{\cdot}1M$ sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Zusammenfassung—Die Metallchelate von Zr(IV) und Th(IV) mit Asparaginsäure und Glutaminsäure wurden potentiometrisch untersucht. Die Bildungskonstanten der einzelnen Stufen in $0{,}1M$ Natriumperchlorat bei 25° werden mitgeteilt: Asparaginsäure-Chelate—log K_1 9,70, log K_2 6,85, log K_3 3,50 für Zr und log K_1 9,23, log K_2 8,57, log K_3 4,55, log K_4 3,87 für Th; Glutaminsäure-Chelate—log K_1 9,60, log K_2 6,40, log K_3 3,32 für Zr und log K_1 9,11, log K_2 8,52, log K_3 4,18, log K_4 3,62 für Th.

Résumé—Les chèlates mètalliques de Zr(IV) et Th(IV) avec les acides aspartique et glutamique ont ètè ètudiès potentiomètriquement. Les constantes de stabilitè par palier en perchlorate de sodium 0,1 M à 25° sont: chèlates aspartiques—log K_1 9,70; log K_2 6,85; et log K_3 3,50 pour Zr et log K_1 9,23; log K_2 8,57, log K_3 4,55 et log K_4 3,87 pour Th; chèlates glutamiques—log K_1 9,60, log K_2 6,40 et log K_3 3,32 pour Zr et log K_1 9,11; log K_2 8,52; log K_3 4,18 et log K_4 3,62 pour Th.

REFERENCES

1. S. Chaberek, Jr. and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 6021.
2. N. C. Li and E. Doody, *ibid.*, 1952, **74**, 4184.
3. R. E. Lumb and A. E. Martell, *J. Phys. Chem.*, 1953, **57**, 690.
4. M. Batyaev, S. V. Larionov and V. M. Shul'man, *Zh. Neorgan. Khim.*, 1961, **6**, 153.
5. M. Cefola, A. S. Tompa, A. V. Celiano and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290.
6. E. E. Kriss, *Ukr. Khim. Zh.*, 1964 **31**, 328.
7. H. Mizuochi, S. Shirakata, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1970, **43**, 397.
8. M. K. Singh and M. N. Srivastava, *Vij. Pari. Anu. Patrika*, in the press.
9. *Idem*, *J. Inorg. Nucl. Chem.*, in the press.
10. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
11. H. Irving and H. S. Rossotti, *J, Chem. Soc.*, 1953, 3397; 1954, 2904.
12. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 106. McGraw-Hill, New York, 1961.

Talanta, 1972, Vol. 19, pp. 700 to 706. Pergamon Press. Printed in Northern Ireland

Thermodynamic dissociation constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid

(*Received* 23 *June* 1971. *Accepted* 17 *November* 1971)

THE pK VALUES of benzohydroxamic acid and substituted phenylbenzohydroxamic acids have been determined in 10–50% v/v dioxan-water media at 25° and 30°. The van Uitert and Haas relation[1] was used to obtain the hydrogen ion concentration from the values read on the pH-meter:

$$-\log\,[\mathrm{H}^+] = \mathrm{pH} + \log U_{\mathrm{H}}{}^0 - \log \frac{1}{\gamma_\pm}$$

The mean activity coefficients were obtained from Harned and Owen[2] and U_H^0 was measured experimentally. It was assumed that the mean activity coefficients were the same on both the molal and molar scales. For aqueous organic media the dissociation constant K is given by

$$pK = pH + \log U_H^0 + \log \frac{[HA]}{[A]} + \log \frac{1}{\gamma_\pm}$$

Hydrolysis of the salt in aqueous medium was taken into consideration[3] *via* the equation

$$pK_{(aq)} = -\log [H^+] + \log \frac{[HA] + [OH^-]}{[A^-] - [OH^-]} + 2 \log \frac{1}{\gamma_\pm}$$

and for mixed aqueous-organic media by

$$pK = pH + \log U_H^0 + \log \frac{[HA] + [OH]}{[A^-] - [OH^-]} + \log \frac{1}{\gamma_\pm}$$

The standard free energy change was calculated in the usual way from pK, and the standard enthalpy change was obtained by integration of the van't Hoff equation at two temperatures. The results are approximate because the heats of ionization vary with temperature, but for the small temperature interval used (10°) $\Delta H°$ may be considered constant.[4] The standard entropy change was obtained from $\Delta G°$ and $\Delta H°$.

EXPERIMENTAL

All the chemicals used were of general or analytical-reagent grade unless otherwise stated. Benzohydroxamic acid was prepared by the method of Hauser and Renfrow[5] and the other hydroxamic acids by the method of Priyadarshini and Tandon.[6] The purity of the acids was established by m.p., elemental analysis and ultraviolet and infrared spectroscopy. Dioxan was purified according to Weissberger.[7] Carbonate-free potassium hydroxide solution was prepared by Vogel's electrolytic method[8] and standardized against potassium hydrogen phthalate and diluted to 0·1M with the solvent medium. The glass-distilled water used was tested for carbonate by Kolthoff's method.[9] The Radiometer pH-meter pHM-4c was calibrated (±0·01 pH unit) with aqueous standard buffer.[10]

The tritation procedure was essentially that recommended by Albert and Serjeant.[11] Generally, 0·01M hydroxamic acid was titrated without addition of inert salts (unadjusted ionic strength). To find the effect of dilution, a few titrations were performed on 0·008–0·012M hydroxamic acid. In the titration vessel (controlled to ±0·1°) 0·5 mmole of hydroxamic acid in 47·5 ml of solvent was titrated with 0·5-ml increments of alkali, after being deaerated by passage of nitrogen (presaturated with solvent) for 15 min, the highest steady pH value being noted after each increment.

RESULTS

Titration of perchloric acid in the presence and absence of the hydroxamic acids showed that the protonation of these acids is very low, as found by others.[12,13] The pK values in various media are shown in Table I. The average error in pK is generally 0·02 but does not exceed 0·03. The pK values were plotted against n, the mole fraction of dioxan, and the empirical relationships derived are shown in Table II. The thermodynamic functions are summarized in Table III.

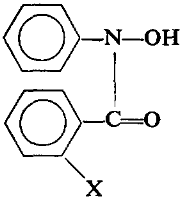
DISCUSSION

The acidity of the hydroxamic acids may be attributed essentially to the —OH group, and the basic character of the nitrogen atom is suppressed as it is in amides. Hydroxamic acids are very weak, though several times stronger than phenol. The suppression of acidic character may be attributed to intramolecular hydrogen-bonding, as shown by infrared studies.[14–16]

Effect of the medium

A solvent of low dielectric constant increases the electrostatic forces between the ions and facilitates formation of molecular species, and should increase pK, as borne out for hydroxamic acids by Tables I and II. Gurney[17] and others[18,19] have pointed out that the standard free energy change of proton transfer may be considered in two parts—electrostatic and non-electrostatic ($\Delta G_{el}°$ and ΔG°_{non}).

TABLE I.—THERMODYNAMIC pK OF BENZOHYDROXAMIC ACID AND ORTHO-SUBSTITUTED N-PHENYLBENZOHYDROXAMIC ACIDS AT 25°C AND 35°C IN DIOXAN-WATER MEDIA



X	Dioxan, % v/v					
	10	20	30	40	45	50
CH$_3$O	8·84	9·24	9·81	10·36	10·70	11·09
	(8·78)*	(9·21)	(9·70)	(10·27)	(10·66)	(11·03)
CH$_3$†	—	9·12	9·61	10·18	—	10.90
	(8·58)	(9·07)	(9·45)	(10·12)	(10·40)	(10·82)
H†	8·85	9·23	9·76	10·30	10·63	11·04
	(8·74)	(9·13)	(9·63)	(10·20)	—	(10·96)
F	8·51	8·92	9·42	10·00	10·34	10·74
	(8·43)	(8·83)	(9·32)	(9·89)	(10·26)	(10·67)
Cl	8·43	8·85	9·35	9·93	10·28	10·67
	(8·31)	(8·79)	(9·23)	(9·81)	(10·14)	(10·56)
Br	8·45	8·86	9·36	9·96	10·30	10·66
	(8·34)	(8·76)	(9·26)	(9·84)	(10·20)	(10·58)
I	‡	8·92	9·41	10·00	10·35	10·75
	‡	(8·80)	(9·30)	(9·90)	(10·25)	(10·63)
NO$_2$	‡	8·87	9·39	10·01	10·37	10·80
	‡	(8·78)	(9·29)	(9·95)	(10·29)	(10·69)
Dielectric constant	68·5	60·5	51·8	42·5	37·5	33·0
Benzohydroxamic acids	9·17	9·45	9·79	10·14	10·41	10·69
	(9·02)	(9·29)	(9·64)	(10·03)	(10·26)	(10·57)

* Values in parenthesis are at 35°.
† Values by Shukla.[12]
‡ Hydroxamic acid insoluble.
§ pK = 8·91 at 25° and 8·79 at 35° in aqueous medium.

TABLE II.—EMPIRICAL RELATIONSHIP BETWEEN pK AND MOLE FRACTION (n) OF DIOXAN

Ortho-substituent X	25°C			35°C		
	p$K = mn + C$		r	p$K = mn + C$		r
	m	C		m	C	
CH$_3$O	14·90	8·52	0·998	14·90	8·45	1·001
CH$_3$	14·09	8·44*	—	14·60	8·28	0·998
H	14·95	8·46*	0·999	14·95	8·36*	0·999
F	14·75	8·18	0·998	14·75	8·09	1·000
Cl	14·65	8·12	0·999	14·65	8·01	0·999
Br	14·80	8·12	0·975	14·85	8·01	0·998
I	14·85	8·17	1·000	14·85	8·07	1·020
NO$_2$	15·35	8·11	1·006	15·35	8·03	0·999
Benzohydroxamic acid	10·10	8·92	0·999	10·10	8·79	0·999

* Calculated from Shukla's results.[12]

TABLE III.—FREE ENERGY, ENTHALPY AND ENTROPY CHANGES FOR IONIZATION OF HYDROXAMIC ACIDS

Substituent	Dioxan, % *v*/*v*						
X	0	10	20	30	40	45	50
OCH$_3$ ΔG°	(11·62)	12·60	12·61	13·39	14·14	14·60	15·13
	(11·91)	12·38	12·99	13·68	14·48	15·03	15·55
(ΔH° 2·9) $-\Delta S^\circ$	(29·1)	30·6	32·4	35·0	37·6	39·1	40·9
	(29·1)	30·6	32·6	34·9	37·4	39·2	40·9
CH$_3$ ΔG°	(11·52)	—	12·45*	13·11*	13·89*	—	14·87*
	(11·68)	12·10	12·78	13·32	14·27	14·67	15·26
(ΔH° 6·7) $-\Delta S^\circ$	(16·1)	—	19·2*	21·4*	24·0*	—	27·3*
	(16·1)	17·4	19·6	21·4	24·5	25·7	27·7
H* ΔG°	11·42	12·08	12·60	13·32	14·00	—	15·06
	11·69	12·32	12·87	13·58	14·38	—	15·67
(ΔH° 4·2) $-\Delta S^\circ$	24·2	26·4	28·1	30·6	32·8	—	36·4
	24·3	26·3	28·1	30·4	33·0	—	36·5
F ΔG°	(11·16)	11·61	12·17	12·85	13·65	14·12	14·65
	(11·40)	11·89	12·46	13·14	13·95	14·46	15·03
(ΔH° 2·8) $-\Delta S^\circ$	(24·7)	26·2	28·1	30·4	33·1	34·6	36·4
	(24·7)	26·2	28·1	30·3	33·0	34·6	36·5
Cl ΔG°	(11·08)	11·50	12·07	12·76	13·55	14·03	14·55
	(11·29)	11·72	12·39	13·01	13·83	14·30	14·89
(ΔH° 4·6) $-\Delta S^\circ$	(21·6)	23·0	25·0	27·3	29·9	31·5	33·3
	(21·6)	23·0	25·2	27·2	29·9	31·4	33·3
Br ΔG°	(11·08)	11·53	12·09	12·77	13·59	14·05	14·54
	(11·29)	11·75	12·35	13·05	13·88	14·38	14·92
(ΔH° 4·6) $-\Delta S^\circ$	(21·6)	23·1	25·0	27·3	30·0	31·6	33·2
	(21·6)	23·1	25·0	27·3	30·0	31·6	33·4
I ΔG°	(11·14)	Insol.	12·17	12·84	13·64	14·12	14·67
	(11·38)	Insol.	12·41	13·11	13·96	14·45	14·98
(ΔH° 4·2) $-\Delta S^\circ$	(23·2)	Insol.	26·7	28·9	31·6	33·2	35·0
	(23·3)	Insol.	26·6	28·9	31·6	33·2	34·9
NO$_2$ ΔG°	(11·06)	Insol.	12·10	12·81	13·66	14·15	14·73
	(11·32)	Insol.	12·38	13·10	14·03	14·51	15·07
(ΔH° 3·4) $-\Delta S^\circ$	(25·8)	Insol.	29·3	31·6	34·5	36·2	38·1
	(25·8)	Insol.	29·2	31·6	34·6	36·1	38·0
Benzohydroxamic acid ΔG°	(12·15)	12·61	12·89	13·36	13·83	14·20	14·58
	12·40	12·72	13·10	13·59	14·14	14·46	14·90
(ΔH° 5·5) $-\Delta S^\circ$	22·4	23·6	24·9	26·5	28·0	29·3	30·6
	22·5	23·5	24·8	26·3	28·1	29·2	30·6

ΔG° and ΔH° in kcal/mole; ΔS° in cal/mole/K; first value at 25°C, second at 35°C.
Values in brackets were obtained by extrapolation.
* From Shukla.[12]

The electrostatic contribution is often estimated from the Born equation[20]

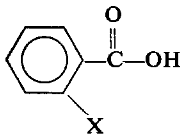
$$\Delta G_{\mathrm{el}}^\circ = \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

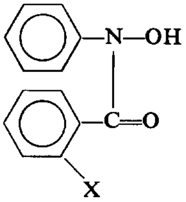
where r_+ and r_- are the radii of the ions and for dilute solutions D is taken as the dielectric constant of the solvent.[21,22] Hence

$$\mathrm{p}K = \frac{\Delta G^\circ_{\mathrm{non}}}{2{\cdot}303RT} + \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

Conventionally, p*K* is plotted *vs.* $1/D$, with $\Delta G^\circ_{\mathrm{non}}$ assumed independent of the solvent. Nearly linear relationships have been reported,[23–26] especially for water-rich media, but so has non-linearity.[27] The plots for the hydroxamic acids are distinctly curved and evidently non-electrostatic factors exert a considerable influence on the dissociation.

TABLE IV.—THERMODYNAMIC IONIZATION CONSTANTS IN AQUEOUS MEDIUM AT 25°C





X	pK	
	Benzoic acids[31]	Hydroxamic acids
H	4·20	8·46
CH_3O	4·09	8·52
CH_3	3·91	8·44
F	3·27	8·18
Cl	2·94	8·12
Br	2·85	8·12
I	2·86	8·17
HO_2	2·17	8·11

The change in p*K* with mole fraction of dioxan is considerable for all the hydroxamic acids, the difference being >2 for water media containing 0 and 50% dioxan.

Thermodynamic functions

The p*K* values were determined with a precision between 0·02 and 0·03, and hence the error in $\Delta G°$ is estimated to be between 0·03 and 0·04 kcal/mole. The method used to compute $\Delta H°$ is subject to large error because the enthalpy change is small and p*K* was not determined at a series of temperatures, which would have allowed use of a more precise method.[28] In our case, an error of 0·01 in ΔpK causes an error of 0·42 kcal/mole in $\Delta H°$, and the magnitude of error in ΔpK depends on the cancellation or addition of errors in the individual p*K* values determined at the two temperatures. However, the positive value of $\Delta H°$ found for all solvent media and acids studies here indicates that the ionization process at temperatures up to 25° is endothermic. Further, the change in $\Delta H°$ with change in medium is relatively small and within experimental error. For this reason the plots of p*K* *vs*. *n* give practically the same slopes at both temperatures (except for *N*-phenyl-*o*-methylbenzohydroxamic acid, for which the results were obtained by others).

It is therefore justifiable to assume that $\Delta H°$ is independent of solvent composition over the range studied. On this basis fresh $\Delta H°$ values were computed from 42 times the difference in the intercepts on the p*K* axis for the p*K*/*n* plots, and it is these values that are given in Table III. The $\Delta S°$ values were also assumed to be independent of solvent composition.

If an acid ionizes in two media, the free energy change for the transfer reaction from one medium to the other is given by 2·303*RT* Δp*K*. For example, with benzohydroxamic acid, $\Delta G°$ is 12·15 and 14·58 kcal/mole for water and 50% aqueous dioxan respectively, and $\Delta G°$ changes by 2·43 kcal/mole in the transfer reaction

$$HA_{(diox)} + H^+_{(ag)} + A^-_{(ag)} \rightleftharpoons HA_{(aq)} + H^+_{(diox)} + A^-_{(diox)}$$

and this is essentially due to a change of $-8{\cdot}2$ cal.mole^{-1} . K^{-1} in $\Delta S°$.

Substituent effects

In the benzoic acid series, regardless of electronic type, nearly all the substituents are acid-strengthening in the *ortho*-position[29] but may be either acid-weakening or strengthening when they are in the *meta*- or *para*-positions, depending on their character. In the *ortho*-substituted phenylbenzohydroxamic acids the acid-strengthening effect is also observed in all cases except methoxy substitution, but it is less than for the corresponding carboxylic acids (Table IV). Like the parent benzoic acid, these *o*-substituted hydroxamic acids do not obey the Hammett equation.[30]

Department of Chemistry
Govt. Science College
Raipur (M.P.), India

Y. K. AGRAWAL*
S. G. TANDON

Summary—Thermodynamic association constants of benzohydroxamic acid and several *ortho*-substituted *N*-phenylbenzohydroxamic acids have been determined by pH titration in aqueous dioxan media at 25° and 35°. Empirical pH corrections for mixed aqueous media have been applied. The pK_a values do not vary linearly with the reciprocal of dielectric constant of the medium, but a plot of pK_a *vs.* the mole fraction of dioxan is linear at a given temperature. Values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are tabulated.

Zusammenfassung—Die thermodynamischen Assoziationskonstanten von Benzhydroxamsäure und mehreren *ortho*-substituierten *N*-Phenylbenzhydroxamsäuren wurden durch pH-Titration in wäßrigen Dioxanmedien bei 25° und 35° ermittelt. Empirische Korrekturen für gemischte wäßrige Medien wurden angebracht. Die pK_a Werte ändern sich nicht linear mit der reziproken Dielektrizitätskonstante des Mediums, aber pK_a gegen den Molenbruch von Dioxan aufgetragen ergibt bei einer gegebenen Temperatur eine Gerade. Die Werte von $\Delta G°$, $\Delta H°$ und $\Delta S°$ sind tabelliert.

Résumé—On a déterminé les constantes d'association thermodynamique de l'acide benzhydroxamique et de plusieurs acides N-phénylbenzhydroxamiques *ortho*-substitués par titrage pH en milieux dioxane aqueux à 25° et 35°. On a appliqué des corrections empiriques de pH pour les milieux aqueux mixtes. Les valeurs de pK_a ne varient pas linéairement avec l'inverse de la constante diélectrique du milieu, mais une courbe du pK_a en fonction de la fraction molaire de dioxane est linéaire à une température donnée. On indique dans une table les valeurs de $\Delta G°$, $\Delta H°$ et $\Delta S°$.

REFERENCES

1. L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 1953, **75**, 451.
2. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd Ed., p. 717. Reinhold, New York, 1958.
3. H. T. S. Britton, *Hydrogen Ions*, 4th Ed., Vol. I, p. 197. Chapman and Hall, London, 1955.
4. S. H. Maron and C. F. Prutton, *Principles of Physical Chemistry*, 4th Ed., p. 249. Macmillan, London, 1966.
5. C. R. Houser and J. R. Renfrow, *Org. Synth. Coll. Vol. II*, p. 67.
6. U. Pryadarshini and S. G. Tandon, *J. Chem. Eng. Data*, 1967, **12**, 143.
7. A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops Jr., *Technique of Organic Chemistry*, Vol. VII, p. 126. Interscience, New York, 1955.
8. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 241. Longmans, London, 1961.
9. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, p. 517. 3rd Ed., Macmillan, London, 1952.
10. R. A. Robinson and R. H. Stokes, *Electrolytic Solutions*, p. 351. Butterworths, London, 1955.
11. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases*, p. 28. Metheun, London, 1962.
12. J. P. Shukla, *Ph.D. Thesis*, Jabalpur University, 1968.
13. G. A. Brydon and D. E. Ryan, *Anal. Chim. Acta*, 1966, **35**, 190.
14. D. Hadži and D. Prevoršek, *Spectrochim. Acta*, 1957, **10**, 38.
15. A. T. Pilipenko, E. A. Shpak and L. Shevchenko, *Russ. J. Inorg. Chem.*, 1967, **12**, 237.
16. O. Exner and J. Holubek, *Collection Czech. Chem. Commun.*, 1966, **30**, 940.
17. R. W. Gurney, *J. Chem. Phys.*, 1938, **6**, 499.
18. E. E. Sager, R. A. Robinson and R. G. Bates, *J. Res. Natl. Bur. Stds.*, 1964, **68A**, 305.
19. E. C. Baughan, *J. Chem. Phys.*, 1939, **7**, 951.
20. M. Born, *Z. Phys.*, 1920, **1**, 45.
21. M. Mandel, *Bull. Soc. Chim. Belg.*, 1955, **64**, 442.
22. M. Mandel and A. Jenard, *ibid.*, 1958, **67**, 575.

23. T. Shedlovsky, in B. Pesce, ed., *Electrolytes*, p. 146. Pergamon, Oxford, 1962.
24. M. Kilpatrick, *Chem. Revs.*, 1942, **30**, 159.
25. R. G. Bates, in B. Pesce, ed., *Electrolytes*, p. 196. Pergamon, Oxford, 1962.
26. C. C. Lynch and V. K. La Mer, *J. Am. Chem. Soc.*, 1938, **60**, 1252.
27. H. S. Harned, *J. Phys. Chem.*, 1939, **43**, 275.
28. J. Lewis and R. G. Wilkins, *Nodern Coordination Chemistry*, p. 18. Interscience, New York, 1960.
29. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 144. Cornell Univ. Press, New York, 1953.
30. R. W. Taft, in *Steric Effects in Organic Chemistry*, ed. M. S. Newman, p. 651. Wiley, New York, 1965.
31. H. C. Brown, D. H. McDaniel and O. Haflinger, in *Determination of Organic Structure by Physical Methods*, eds. E. A. Branch and F. C. Nachod, Chapter 14. Academic Press, New York, 1965.

Talanta, 1972, Vol. 19, pp. 706 to 707. Pergamon Press. Printed in Northern Ireland

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions

(*Received* 21 *October* 1971. *Accepted* 14 *December* 1971)

THE COMPLEXATION of thiodipropionic acid (TDPA) with indium(III) and uranium(VI) has been studied by the methods used earlier.[1,2] Polarographic waves were recorded with a manual polarograph at 30 ± 0.1° using an H-cell with a saturated calomel electrode as reference electrode. The DME had the characteristics $m = 2.74$ mg/sec, $t = 3.20$ sec.

Experiments were performed with 0.25m*M* indium or uranium and 0.025–0.30*M* TDPA at an ionic strength of 1.2*M* (potassium chloride) for In and in 0.01*M* hydrochloric acid/0.1*M* potassium chloride for uranium (to obtain diffusion-controlled, reversible one-electron reduction of U(VI) at the DME).

The results were interpreted by means of the Deford and Hume[3] and the Irving[4] methods.

RESULTS AND DISCUSSION

Indium–TDPA

The reduction of indium–TDPA complex at the DME gives a well-defined diffusion controlled reversible 3-electron wave in aqueous and in aqueous methanol solutions. The half-wave potential increases slightly at pH values from 1.5 to 3, then more sharply till the pH reaches 5.0, above which precipitation takes place.

The presence of 10%, 30% and 50% methanol yields a well-defined wave with $E_{1/2} = -0.600$, -0.614 and -0.614 V *vs.* SCE respectively, $E_{1/2}$ is -0.6025 V for indium(III) in aqueous solution. This rules out complexation between the metal ions and methanol. A negative shift in $E_{1/2}$ on addition of increasing amounts of TDPA indicates complex formation.

The overall stability constants are summarized in Table I. Increasing the methanol concentration considerably increases the stability constants.

TABLE I.—STABILITY CONSTANTS FOR In(III)-TDPA SYSTEM

Methanol conc. of the media %	β_1	β_2	β_3	β_4
0	20	80	2.4×10^2	2.6×10^3
10	31	80	2.6×10^2	2.8×10^3
30	44	2.1×10^2	4.3×10^2	3.4×10^3
50	120	3.0×10^2	12.0×10^2	17.8×10^3

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in 0·1*M* sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Zusammenfassung—Die Metallchelate von Zr(IV) und Th(IV) mit Asparaginsäure und Glutaminsäure wurden potentiometrisch untersucht. Die Bildungskonstanten der einzelnen Stufen in 0,1*M* Natriumperchlorat bei 25° werden mitgeteilt: Asparaginsäure-Chelate—log K_1 9,70, log K_2 6,85, log K_3 3,50 für Zr und log K_1 9,23, log K_2 8,57, log K_3 4,55, log K_4 3,87 für Th; Glutaminsäure-Chelate—log K_1 9,60, log K_2 6,40, log K_3 3,32 für Zr und log K_1 9,11, log K_2 8,52, log K_3 4,18, log K_4 3,62 für Th.

Résumé—Les chèlates mètalliques de Zr(IV) et Th(IV) avec les acides aspartique et glutamique ont ètè ètudiès potentiomètriquement. Les constantes de stabilitè par palier en perchlorate de sodium 0,1 *M* à 25° sont: chèlates aspartiques—log K_1 9,70; log K_2 6,85; et log K_3 3,50 pour Zr et log K_1 9,23; log K_2 8,57, log K_3 4,55 et log K_4 3,87 pour Th; chèlates glutamiques—log K_1 9,60, log K_2 6,40 et log K_3 3,32 pour Zr et log K_1 9,11; log K_2 8,52; log K_3 4,18 et log K_4 3,62 pour Th.

REFERENCES

1. S. Chaberek, Jr. and A. E. Martell, *J. Am. Chem. Soc.*, 1952, **74**, 6021.
2. N. C. Li and E. Doody, *ibid.*, 1952, **74**, 4184.
3. R. E. Lumb and A. E. Martell, *J. Phys. Chem.*, 1953, **57**, 690.
4. M. Batyaev, S. V. Larionov and V. M. Shul'man, *Zh. Neorgan. Khim.*, 1961, **6**, 153.
5. M. Cefola, A. S. Tompa, A. V. Celiano and P. S. Gentile, *Inorg. Chem.*, 1962, **1**, 290.
6. E. E. Kriss, *Ukr. Khim. Zh.*, 1964 **31**, 328.
7. H. Mizuochi, S. Shirakata, E. Kyuno and R. Tsuchiya, *Bull. Chem. Soc. Japan*, 1970, **43**, 397.
8. M. K. Singh and M. N. Srivastava, *Vij. Pari. Anu. Patrika*, in the press.
9. *Idem*, *J. Inorg. Nucl. Chem.*, in the press.
10. M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, 1945, **67**, 2003.
11. H. Irving and H. S. Rossotti, *J, Chem. Soc.*, 1953, 3397; 1954, 2904.
12. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 106. McGraw-Hill, New York, 1961.

Talanta, 1972, Vol. 19, pp. 700 to 706. Pergamon Press. Printed in Northern Ireland

Thermodynamic dissociation constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid

(*Received* 23 *June* 1971. *Accepted* 17 *November* 1971)

THE p*K* VALUES of benzohydroxamic acid and substituted phenylbenzohydroxamic acids have been determined in 10–50% v/v dioxan-water media at 25° and 30°. The van Uitert and Haas relation[1] was used to obtain the hydrogen ion concentration from the values read on the pH-meter:

$$-\log\,[\mathrm{H}^+] = \mathrm{pH} + \log U_{\mathrm{H}}{}^0 - \log\frac{1}{\gamma_\pm}$$

The mean activity coefficients were obtained from Harned and Owen[2] and U_H^0 was measured experimentally. It was assumed that the mean activity coefficients were the same on both the molal and molar scales. For aqueous organic media the dissociation constant K is given by

$$pK = pH + \log U_H^0 + \log \frac{[HA]}{[A]} + \log \frac{1}{\gamma_\pm}$$

Hydrolysis of the salt in aqueous medium was taken into consideration[3] *via* the equation

$$pK_{(aq)} = -\log [H^+] + \log \frac{[HA] + [OH^-]}{[A^-] - [OH^-]} + 2 \log \frac{1}{\gamma_\pm}$$

and for mixed aqueous-organic media by

$$pK = pH + \log U_H^0 + \log \frac{[HA] + [OH]}{[A^-] - [OH^-]} + \log \frac{1}{\gamma_\pm}$$

The standard free energy change was calculated in the usual way from pK, and the standard enthalpy change was obtained by integration of the van't Hoff equation at two temperatures. The results are approximate because the heats of ionization vary with temperature, but for the small temperature interval used (10°) $\Delta H°$ may be considered constant.[4] The standard entropy change was obtained from $\Delta G°$ and $\Delta H°$.

EXPERIMENTAL

All the chemicals used were of general or analytical-reagent grade unless otherwise stated. Benzohydroxamic acid was prepared by the method of Hauser and Renfrow[5] and the other hydroxamic acids by the method of Priyadarshini and Tandon.[6] The purity of the acids was established by m.p., elemental analysis and ultraviolet and infrared spectroscopy. Dioxan was purified according to Weissberger.[7] Carbonate-free potassium hydroxide solution was prepared by Vogel's electrolytic method[8] and standardized against potassium hydrogen phthalate and diluted to 0·1M with the solvent medium. The glass-distilled water used was tested for carbonate by Kolthoff's method.[9] The Radiometer pH-meter pHM-4c was calibrated (±0·01 pH unit) with aqueous standard buffer.[10]

The tritation procedure was essentially that recommended by Albert and Serjeant.[11] Generally, 0·01M hydroxamic acid was titrated without addition of inert salts (unadjusted ionic strength). To find the effect of dilution, a few titrations were performed on 0·008–0·012M hydroxamic acid. In the titration vessel (controlled to ±0·1°) 0·5 mmole of hydroxamic acid in 47·5 ml of solvent was titrated with 0·5-ml increments of alkali, after being deaerated by passage of nitrogen (presaturated with solvent) for 15 min, the highest steady pH value being noted after each increment.

RESULTS

Titration of perchloric acid in the presence and absence of the hydroxamic acids showed that the protonation of these acids is very low, as found by others.[12,13] The pK values in various media are shown in Table I. The average error in pK is generally 0·02 but does not exceed 0·03. The pK values were plotted against n, the mole fraction of dioxan, and the empirical relationships derived are shown in Table II. The thermodynamic functions are summarized in Table III.

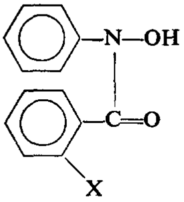
DISCUSSION

The acidity of the hydroxamic acids may be attributed essentially to the —OH group, and the basic character of the nitrogen atom is suppressed as it is in amides. Hydroxamic acids are very weak, though several times stronger than phenol. The suppression of acidic character may be attributed to intramolecular hydrogen-bonding, as shown by infrared studies.[14–16]

Effect of the medium

A solvent of low dielectric constant increases the electrostatic forces between the ions and facilitates formation of molecular species, and should increase pK, as borne out for hydroxamic acids by Tables I and II. Gurney[17] and others[18,19] have pointed out that the standard free energy change of proton transfer may be considered in two parts—electrostatic and non-electrostatic ($\Delta G_{el}°$ and $\Delta G°_{non}$).

TABLE I.—THERMODYNAMIC p*K* OF BENZOHYDROXAMIC ACID AND ORTHO-SUBSTITUTED *N*-PHENYLBENZOHYDROXAMIC ACIDS AT 25°C AND 35°C IN DIOXAN-WATER MEDIA



X	Dioxan, % *v*/*v*					
	10	20	30	40	45	50
CH$_3$O	8·84	9·24	9·81	10·36	10·70	11·09
	(8·78)*	(9·21)	(9·70)	(10·27)	(10·66)	(11·03)
CH$_3$†	—	9·12	9·61	10·18	—	10.90
	(8·58)	(9·07)	(9·45)	(10·12)	(10·40)	(10·82)
H†	8·85	9·23	9·76	10·30	10·63	11·04
	(8·74)	(9·13)	(9·63)	(10·20)	—	(10·96)
F	8·51	8·92	9·42	10·00	10·34	10·74
	(8·43)	(8·83)	(9·32)	(9·89)	(10·26)	(10·67)
Cl	8·43	8·85	9·35	9·93	10·28	10·67
	(8·31)	(8·79)	(9·23)	(9·81)	(10·14)	(10·56)
Br	8·45	8·86	9·36	9·96	10·30	10·66
	(8·34)	(8·76)	(9·26)	(9·84)	(10·20)	(10·58)
I	‡	8·92	9·41	10·00	10·35	10·75
	‡	(8·80)	(9·30)	(9·90)	(10·25)	(10·63)
NO$_2$	‡	8·87	9·39	10·01	10·37	10·80
	‡	(8·78)	(9·29)	(9·95)	(10·29)	(10·69)
Dielectric constant	68·5	60·5	51·8	42·5	37·5	33·0
Benzohydroxamic acids	9·17	9·45	9·79	10·14	10·41	10·69
	(9·02)	(9·29)	(9·64)	(10·03)	(10·26)	(10·57)

* Values in parenthesis are at 35°.

† Values by Shukla.[12]

‡ Hydroxamic acid insoluble.

§ p*K* = 8·91 at 25° and 8·79 at 35° in aqueous medium.

TABLE II.—EMPIRICAL RELATIONSHIP BETWEEN p*K* AND MOLE FRACTION (*n*) OF DIOXAN

Ortho-substituent X	25°C			35°C		
	p*K* = *mn* + *C*		*r*	p*K* = *mn* + *C*		*r*
	m	*C*		*m*	*C*	
CH$_3$O	14·90	8·52	0·998	14·90	8·45	1·001
CH$_3$	14·09	8·44*	—	14·60	8·28	0·998
H	14·95	8·46*	0·999	14·95	8·36*	0·999
F	14·75	8·18	0·998	14·75	8·09	1·000
Cl	14·65	8·12	0·999	14·65	8·01	0·999
Br	14·80	8·12	0·975	14·85	8·01	0·998
I	14·85	8·17	1·000	14·85	8·07	1·020
NO$_2$	15·35	8·11	1·006	15·35	8·03	0·999
Benzohydroxamic acid	10·10	8·92	0·999	10·10	8·79	0·999

* Calculated from Shukla's results.[12]

TABLE III.—FREE ENERGY, ENTHALPY AND ENTROPY CHANGES FOR IONIZATION OF HYDROXAMIC ACIDS

Substituent	Dioxan, % *v*/*v*						
X	0	10	20	30	40	45	50
OCH$_3$ ΔG°	(11·62)	12·60	12·61	13·39	14·14	14·60	15·13
	(11·91)	12·38	12·99	13·68	14·48	15·03	15·55
(ΔH° 2·9) $-\Delta S^\circ$	(29·1)	30·6	32·4	35·0	37·6	39·1	40·9
	(29·1)	30·6	32·6	34·9	37·4	39·2	40·9
CH$_3$ ΔG°	(11·52)	—	12·45*	13·11*	13·89*	—	14·87*
	(11·68)	12·10	12·78	13·32	14·27	14·67	15·26
(ΔH° 6·7) $-\Delta S^\circ$	(16·1)	—	19·2*	21·4*	24·0*	—	27·3*
	(16·1)	17·4	19·6	21·4	24·5	25·7	27·7
H* ΔG°	11·42	12·08	12·60	13·32	14·00	—	15·06
	11·69	12·32	12·87	13·58	14·38	—	15·67
(ΔH° 4·2) $-\Delta S^\circ$	24·2	26·4	28·1	30·6	32·8	—	36·4
	24·3	26·3	28·1	30·4	33·0	—	36·5
F ΔG°	(11·16)	11·61	12·17	12·85	13·65	14·12	14·65
	(11·40)	11·89	12·46	13·14	13·95	14·46	15·03
(ΔH° 2·8) $-\Delta S^\circ$	(24·7)	26·2	28·1	30·4	33·1	34·6	36·4
	(24·7)	26·2	28·1	30·3	33·0	34·6	36·5
Cl ΔG°	(11·08)	11·50	12·07	12·76	13·55	14·03	14·55
	(11·29)	11·72	12·39	13·01	13·83	14·30	14·89
(ΔH° 4·6) $-\Delta S^\circ$	(21·6)	23·0	25·0	27·3	29·9	31·5	33·3
	(21·6)	23·0	25·2	27·2	29·9	31·4	33·3
Br ΔG°	(11·08)	11·53	12·09	12·77	13·59	14·05	14·54
	(11·29)	11·75	12·35	13·05	13·88	14·38	14·92
(ΔH° 4·6) $-\Delta S^\circ$	(21·6)	23·1	25·0	27·3	30·0	31·6	33·2
	(21·6)	23·1	25·0	27·3	30·0	31·6	33·4
I ΔG°	(11·14)	Insol.	12·17	12·84	13·64	14·12	14·67
	(11·38)	Insol.	12·41	13·11	13·96	14·45	14·98
(ΔH° 4·2) $-\Delta S^\circ$	(23·2)	Insol.	26·7	28·9	31·6	33·2	35·0
	(23·3)	Insol.	26·6	28·9	31·6	33·2	34·9
NO$_2$ ΔG°	(11·06)	Insol.	12·10	12·81	13·66	14·15	14·73
	(11·32)	Insol.	12·38	13·10	14·03	14·51	15·07
(ΔH° 3·4) $-\Delta S^\circ$	(25·8)	Insol.	29·3	31·6	34·5	36·2	38·1
	(25·8)	Insol.	29·2	31·6	34·6	36·1	38·0
Benzohydroxamic acid ΔG°	(12·15)	12·61	12·89	13·36	13·83	14·20	14·58
	12·40	12·72	13·10	13·59	14·14	14·46	14·90
(ΔH° 5·5) $-\Delta S^\circ$	22·4	23·6	24·9	26·5	28·0	29·3	30·6
	22·5	23·5	24·8	26·3	28·1	29·2	30·6

ΔG° and ΔH° in kcal/mole; ΔS° in cal/mole/K; first value at 25°C, second at 35°C.
Values in brackets were obtained by extrapolation.
* From Shukla.[12]

The electrostatic contribution is often estimated from the Born equation[20]

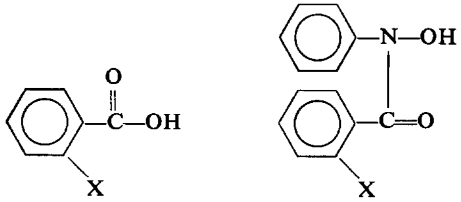
$$\Delta G_{\text{el}}^\circ = \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

where r_+ and r_- are the radii of the ions and for dilute solutions D is taken as the dielectric constant of the solvent.[21,22] Hence

$$\mathrm{p}K = \frac{\Delta G^\circ_{\text{non}}}{2{\cdot}303RT} + \frac{Ne^2}{2D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

Conventionally, pK is plotted *vs.* $1/D$, with $\Delta G^\circ_{\text{non}}$ assumed independent of the solvent. Nearly linear relationships have been reported,[23–26] especially for water-rich media, but so has non-linearity.[27] The plots for the hydroxamic acids are distinctly curved and evidently non-electrostatic factors exert a considerable influence on the dissociation.

TABLE IV.—THERMODYNAMIC IONIZATION CONSTANTS IN AQUEOUS MEDIUM AT 25°C



X	pK	
	Benzoic acids[31]	Hydroxamic acids
H	4·20	8·46
CH_3O	4·09	8·52
CH_3	3·91	8·44
F	3·27	8·18
Cl	2·94	8·12
Br	2·85	8·12
I	2·86	8·17
HO_2	2·17	8·11

The change in p*K* with mole fraction of dioxan is considerable for all the hydroxamic acids, the difference being >2 for water media containing 0 and 50% dioxan.

Thermodynamic functions

The p*K* values were determined with a precision between 0·02 and 0·03, and hence the error in $\Delta G°$ is estimated to be between 0·03 and 0·04 kcal/mole. The method used to compute $\Delta H°$ is subject to large error because the enthalpy change is small and p*K* was not determined at a series of temperatures, which would have allowed use of a more precise method.[28] In our case, an error of 0·01 in Δp*K* causes an error of 0·42 kcal/mole in $\Delta H°$, and the magnitude of error in Δp*K* depends on the cancellation or addition of errors in the individual p*K* values determined at the two temperatures. However, the positive value of $\Delta H°$ found for all solvent media and acids studies here indicates that the ionization process at temperatures up to 25° is endothermic. Further, the change in $\Delta H°$ with change in medium is relatively small and within experimental error. For this reason the plots of p*K* *vs.* *n* give practically the same slopes at both temperatures (except for *N*-phenyl-*o*-methylbenzohydroxamic acid, for which the results were obtained by others).

It is therefore justifiable to assume that $\Delta H°$ is independent of solvent composition over the range studied. On this basis fresh $\Delta H°$ values were computed from 42 times the difference in the intercepts on the p*K* axis for the p*K*/*n* plots, and it is these values that are given in Table III. The $\Delta S°$ values were also assumed to be independent of solvent composition.

If an acid ionizes in two media, the free energy change for the transfer reaction from one medium to the other is given by 2·303*RT* Δp*K*. For example, with benzohydroxamic acid, $\Delta G°$ is 12·15 and 14·58 kcal/mole for water and 50% aqueous dioxan respectively, and $\Delta G°$ changes by 2·43 kcal/mole in the transfer reaction

$$HA_{(diox)} + H^+_{(ag)} + A^-_{(ag)} \rightleftharpoons HA_{(aq)} + H^+_{(diox)} + A^-_{(diox)}$$

and this is essentially due to a change of $-8{\cdot}2$ cal.mole^{-1} . K^{-1} in $\Delta S°$.

Substituent effects

In the benzoic acid series, regardless of electronic type, nearly all the substituents are acid-strengthening in the *ortho*-position[29] but may be either acid-weakening or strengthening when they are in the *meta*- or *para*-positions, depending on their character. In the *ortho*-substituted phenylbenzohydroxamic acids the acid-strengthening effect is also observed in all cases except methoxy substitution, but it is less than for the corresponding carboxylic acids (Table IV). Like the parent benzoic acid, these *o*-substituted hydroxamic acids do not obey the Hammett equation.[30]

Department of Chemistry
Govt. Science College
Raipur (M.P.), India

Y. K. AGRAWAL*
S. G. TANDON

Summary—Thermodynamic association constants of benzohydroxamic acid and several *ortho*-substituted *N*-phenylbenzohydroxamic acids have been determined by pH titration in aqueous dioxan media at 25° and 35°. Empirical pH corrections for mixed aqueous media have been applied. The pK_a values do not vary linearly with the reciprocal of dielectric constant of the medium, but a plot of pK_a *vs.* the mole fraction of dioxan is linear at a given temperature. Values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are tabulated.

Zusammenfassung—Die thermodynamischen Assoziationskonstanten von Benzhydroxamsäure und mehreren *ortho*-substituierten *N*-Phenylbenzhydroxamsäuren wurden durch pH-Titration in wäßrigen Dioxanmedien bei 25° und 35° ermittelt. Empirische Korrekturen für gemischte wäßrige Medien wurden angebracht. Die pK_a Werte ändern sich nicht linear mit der reziproken Dielektrizitätskonstante des Mediums, aber pK_a gegen den Molenbruch von Dioxan aufgetragen ergibt bei einer gegebenen Temperatur eine Gerade. Die Werte von $\Delta G°$, $\Delta H°$ und $\Delta S°$ sind tabelliert.

Résumé—On a déterminé les constantes d'association thermodynamique de l'acide benzhydroxamique et de plusieurs acides N-phénylbenzhydroxamiques *ortho*-substitués par titrage pH en milieux dioxane aqueux à 25° et 35°. On a appliqué des corrections empiriques de pH pour les milieux aqueux mixtes. Les valeurs de pK_a ne varient pas linéairement avec l'inverse de la constante diélectrique du milieu, mais une courbe du pK_a en fonction de la fraction molaire de dioxane est linéaire à une température donnée. On indique dans une table les valeurs de $\Delta G°$, $\Delta H°$ et $\Delta S°$.

REFERENCES

1. L. G. Van Uitert and C. G. Haas, *J. Am. Chem. Soc.*, 1953, **75**, 451.
2. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd Ed., p. 717. Reinhold, New York, 1958.
3. H. T. S. Britton, *Hydrogen Ions*, 4th Ed., Vol. I, p. 197. Chapman and Hall, London, 1955.
4. S. H. Maron and C. F. Prutton, *Principles of Physical Chemistry*, 4th Ed., p. 249. Macmillan, London, 1966.
5. C. R. Houser and J. R. Renfrow, *Org. Synth. Coll. Vol. II*, p. 67.
6. U. Pryadarshini and S. G. Tandon, *J. Chem. Eng. Data*, 1967, **12**, 143.
7. A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops Jr., *Technique of Organic Chemistry*, Vol. VII, p. 126. Interscience, New York, 1955.
8. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 3rd Ed., p. 241. Longmans, London, 1961.
9. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, p. 517. 3rd Ed., Macmillan, London, 1952.
10. R. A. Robinson and R. H. Stokes, *Electrolytic Solutions*, p. 351. Butterworths, London, 1955.
11. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases*, p. 28. Metheun, London, 1962.
12. J. P. Shukla, *Ph.D. Thesis*, Jabalpur University, 1968.
13. G. A. Brydon and D. E. Ryan, *Anal. Chim. Acta*, 1966, **35**, 190.
14. D. Hadži and D. Prevoršek, *Spectrochim. Acta*, 1957, **10**, 38.
15. A. T. Pilipenko, E. A. Shpak and L. Shevchenko, *Russ. J. Inorg. Chem.*, 1967, **12**, 237.
16. O. Exner and J. Holubek, *Collection Czech. Chem. Commun.*, 1966, **30**, 940.
17. R. W. Gurney, *J. Chem. Phys.*, 1938, **6**, 499.
18. E. E. Sager, R. A. Robinson and R. G. Bates, *J. Res. Natl. Bur. Stds.*, 1964, **68A**, 305.
19. E. C. Baughan, *J. Chem. Phys.*, 1939, **7**, 951.
20. M. Born, *Z. Phys.*, 1920, **1**, 45.
21. M. Mandel, *Bull. Soc. Chim. Belg.*, 1955, **64**, 442.
22. M. Mandel and A. Jenard, *ibid.*, 1958, **67**, 575.

23. T. Shedlovsky, in B. Pesce, ed., *Electrolytes*, p. 146. Pergamon, Oxford, 1962.
24. M. Kilpatrick, *Chem. Revs.*, 1942, **30**, 159.
25. R. G. Bates, in B. Pesce, ed., *Electrolytes*, p. 196. Pergamon, Oxford, 1962.
26. C. C. Lynch and V. K. La Mer, *J. Am. Chem. Soc.*, 1938, **60**, 1252.
27. H. S. Harned, *J. Phys. Chem.*, 1939, **43**, 275.
28. J. Lewis and R. G. Wilkins, *Nodern Coordination Chemistry*, p. 18. Interscience, New York, 1960.
29. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 144. Cornell Univ. Press, New York, 1953.
30. R. W. Taft, in *Steric Effects in Organic Chemistry*, ed. M. S. Newman, p. 651. Wiley, New York, 1965.
31. H. C. Brown, D. H. McDaniel and O. Haflinger, in *Determination of Organic Structure by Physical Methods*, eds. E. A. Branch and F. C. Nachod, Chapter 14. Academic Press, New York, 1965.

Talanta, 1972, Vol. 19, pp. 706 to 707. Pergamon Press. Printed in Northern Ireland

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions

(*Received* 21 *October* 1971. *Accepted* 14 *December* 1971)

THE COMPLEXATION of thiodipropionic acid (TDPA) with indium(III) and uranium(VI) has been studied by the methods used earlier.[1,2] Polarographic waves were recorded with a manual polarograph at 30 ± 0.1° using an H-cell with a saturated calomel electrode as reference electrode. The DME had the characteristics $m = 2.74$ mg/sec, $t = 3.20$ sec.

Experiments were performed with 0.25mM indium or uranium and 0.025–0.30M TDPA at an ionic strength of 1.2M (potassium chloride) for In and in 0.01M hydrochloric acid/0.1M potassium chloride for uranium (to obtain diffusion-controlled, reversible one-electron reduction of U(VI) at the DME).

The results were interpreted by means of the Deford and Hume[3] and the Irving[4] methods.

RESULTS AND DISCUSSION

Indium–TDPA

The reduction of indium–TDPA complex at the DME gives a well-defined diffusion controlled reversible 3-electron wave in aqueous and in aqueous methanol solutions. The half-wave potential increases slightly at pH values from 1.5 to 3, then more sharply till the pH reaches 5.0, above which precipitation takes place.

The presence of 10%, 30% and 50% methanol yields a well-defined wave with $E_{1/2} = -0.600$, -0.614 and -0.614 V *vs.* SCE respectively, $E_{1/2}$ is -0.6025 V for indium(III) in aqueous solution. This rules out complexation between the metal ions and methanol. A negative shift in $E_{1/2}$ on addition of increasing amounts of TDPA indicates complex formation.

The overall stability constants are summarized in Table I. Increasing the methanol concentration considerably increases the stability constants.

TABLE I.—STABILITY CONSTANTS FOR In(III)-TDPA SYSTEM

Methanol conc. of the media %	β_1	β_2	β_3	β_4
0	20	80	2.4×10^2	2.6×10^3
10	31	80	2.6×10^2	2.8×10^3
30	44	2.1×10^2	4.3×10^2	3.4×10^3
50	120	3.0×10^2	12.0×10^2	17.8×10^3

23. T. Shedlovsky, in B. Pesce, ed., *Electrolytes*, p. 146. Pergamon, Oxford, 1962.
24. M. Kilpatrick, *Chem. Revs.*, 1942, **30**, 159.
25. R. G. Bates, in B. Pesce, ed., *Electrolytes*, p. 196. Pergamon, Oxford, 1962.
26. C. C. Lynch and V. K. La Mer, *J. Am. Chem. Soc.*, 1938, **60**, 1252.
27. H. S. Harned, *J. Phys. Chem.*, 1939, **43**, 275.
28. J. Lewis and R. G. Wilkins, *Nodern Coordination Chemistry*, p. 18. Interscience, New York, 1960.
29. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 144. Cornell Univ. Press, New York, 1953.
30. R. W. Taft, in *Steric Effects in Organic Chemistry*, ed. M. S. Newman, p. 651. Wiley, New York, 1965.
31. H. C. Brown, D. H. McDaniel and O. Haflinger, in *Determination of Organic Structure by Physical Methods*, eds. E. A. Branch and F. C. Nachod, Chapter 14. Academic Press, New York, 1965.

Talanta, 1972, Vol. 19, pp. 706 to 707. Pergamon Press. Printed in Northern Ireland

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions

(*Received* 21 *October* 1971. *Accepted* 14 *December* 1971)

THE COMPLEXATION of thiodipropionic acid (TDPA) with indium(III) and uranium(VI) has been studied by the methods used earlier.[1,2] Polarographic waves were recorded with a manual polarograph at 30 ± 0.1° using an H-cell with a saturated calomel electrode as reference electrode. The DME had the characteristics $m = 2.74$ mg/sec, $t = 3.20$ sec.

Experiments were performed with 0.25m*M* indium or uranium and 0.025–0.30*M* TDPA at an ionic strength of 1.2*M* (potassium chloride) for In and in 0.01*M* hydrochloric acid/0.1*M* potassium chloride for uranium (to obtain diffusion-controlled, reversible one-electron reduction of U(VI) at the DME).

The results were interpreted by means of the Deford and Hume[3] and the Irving[4] methods.

RESULTS AND DISCUSSION

Indium–TDPA

The reduction of indium–TDPA complex at the DME gives a well-defined diffusion controlled reversible 3-electron wave in aqueous and in aqueous methanol solutions. The half-wave potential increases slightly at pH values from 1.5 to 3, then more sharply till the pH reaches 5.0, above which precipitation takes place.

The presence of 10%, 30% and 50% methanol yields a well-defined wave with $E_{1/2} = -0.600$, -0.614 and -0.614 V *vs.* SCE respectively, $E_{1/2}$ is -0.6025 V for indium(III) in aqueous solution. This rules out complexation between the metal ions and methanol. A negative shift in $E_{1/2}$ on addition of increasing amounts of TDPA indicates complex formation.

The overall stability constants are summarized in Table I. Increasing the methanol concentration considerably increases the stability constants.

TABLE I.—STABILITY CONSTANTS FOR In(III)-TDPA SYSTEM

Methanol conc. of the media %	β_1	β_2	β_3	β_4
0	20	80	2.4×10^2	2.6×10^3
10	31	80	2.6×10^2	2.8×10^3
30	44	2.1×10^2	4.3×10^2	3.4×10^3
50	120	3.0×10^2	12.0×10^2	17.8×10^3

Uranyl–TDPA System

Uranyl ion in TDPA gives a diffusion-controlled reversible one-electron reduction at the DME in aqueous and 30% methanol media.

A negative shift in $E_{1/2}$ coupled with a decrease in diffusion current with increasing concentration of TDPA indicates complexation. The values for β_1, β_2 and β_3 are 3.3, 1.2 and 8.5 in aqueous media; in 30% methanolic media the corresponding values are 5.5, 1.2 and 34. Again addition of methanol increases the stability.

Acknowledgement—We thank Prof. R. C. Mehrotra, University of Rajasthan, Jaipur and Prof. R. M. Advani of M.R.E. College, Jaipur for their interest and provision of research facilities.

Department of Chemistry
M.R.E. College
Jaipur-4, India
P. C. RAWAT

Chemical Laboratories
University of Rajasthan
Jaipur-4, India
C. M. GUPTA

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water–methanol solutions at 30 ± 0·1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in 0·1*M* HCl, with 0·1*M* KCl as supporting electrolyte.

Zusammenfassung—Die Komplexbildung von In(III) und U(VI) mit Thiodipropionsäure wurde polarographisch in Wasser und Wasser-Methanol bei 30 ± 0,1° untersucht. Alle Chelate gehören zu polarographisch reversiblen Systemen. Mit Indium(III) werden bei pH 4,8 Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2, 1:3 und 1:4 gefunden. Uran(VI) bildet in 0,01 M HCl mit 0,1 M KCl als Leitelektrolyt nacheinander drei Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2 und 1:3.

Résumé—On a étudié polarographiquement la complexation de In(III) et U(VI) avec l'acide thiodipropionique en solution dans l'eau et l'eauméthanol à 30 ± 0,1°. Tous les chélates appartiennent à des systèmes réversibles polarographiquement. Avec l'indium(III), on trouve des complexes avec des rapports métal:ligand de 1:1, 1:2, 1:3 et 1:4 à pH 4,8. On trouve que l'uranium(VI) forme trois complexes successifs avec des rapports métal:ligand de 1:1, 1:2 et 1:3 en HCl 0,01*M* avec KCl 0,1*M* comme électrolyte support.

REFERENCES

1. P. C. Rawat and C. M. Gupta, *J. Inorg. Nucl. Chem.*, 1972, **34**, 951.
2. *Idem, ibid.*, 1972, **34**, 1621.
3. D. D. Deford, D. N. Hume, *J. Am. Chem. Soc.*, 1951, **73**, 5321.
4. H. Irving, *Advan. Polarog.*, 1960, **1**, 42.

Talanta, 1972, Vol. 19, pp. 708 to 711. Pergamon Press. Printed in Northern Ireland

Determination of pK_a of acetic and benzoic acids in pyridine

(*Received* 23 *June* 1971. *Accepted* 2 *October* 1971)

FROM AN ANALYSIS of half-neutralization potentials (HNP) in pyridine referred to that of benzoic acid, Streuli and Miron[1] were able to classify a number of organic acids, including certain aliphatic

23. T. Shedlovsky, in B. Pesce, ed., *Electrolytes*, p. 146. Pergamon, Oxford, 1962.
24. M. Kilpatrick, *Chem. Revs.*, 1942, **30**, 159.
25. R. G. Bates, in B. Pesce, ed., *Electrolytes*, p. 196. Pergamon, Oxford, 1962.
26. C. C. Lynch and V. K. La Mer, *J. Am. Chem. Soc.*, 1938, **60**, 1252.
27. H. S. Harned, *J. Phys. Chem.*, 1939, **43**, 275.
28. J. Lewis and R. G. Wilkins, *Nodern Coordination Chemistry*, p. 18. Interscience, New York, 1960.
29. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, p. 144. Cornell Univ. Press, New York, 1953.
30. R. W. Taft, in *Steric Effects in Organic Chemistry*, ed. M. S. Newman, p. 651. Wiley, New York, 1965.
31. H. C. Brown, D. H. McDaniel and O. Haflinger, in *Determination of Organic Structure by Physical Methods*, eds. E. A. Branch and F. C. Nachod, Chapter 14. Academic Press, New York, 1965.

Talanta, 1972, Vol. 19, pp. 706 to 707. Pergamon Press. Printed in Northern Ireland

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions

(*Received* 21 *October* 1971. *Accepted* 14 *December* 1971)

THE COMPLEXATION of thiodipropionic acid (TDPA) with indium(III) and uranium(VI) has been studied by the methods used earlier.[1,2] Polarographic waves were recorded with a manual polarograph at 30 ± 0.1° using an H-cell with a saturated calomel electrode as reference electrode. The DME had the characteristics $m = 2.74$ mg/sec, $t = 3.20$ sec.

Experiments were performed with 0.25mM indium or uranium and 0.025–0.30M TDPA at an ionic strength of 1.2M (potassium chloride) for In and in 0.01M hydrochloric acid/0.1M potassium chloride for uranium (to obtain diffusion-controlled, reversible one-electron reduction of U(VI) at the DME).

The results were interpreted by means of the Deford and Hume[3] and the Irving[4] methods.

RESULTS AND DISCUSSION

Indium–TDPA

The reduction of indium–TDPA complex at the DME gives a well-defined diffusion controlled reversible 3-electron wave in aqueous and in aqueous methanol solutions. The half-wave potential increases slightly at pH values from 1.5 to 3, then more sharply till the pH reaches 5.0, above which precipitation takes place.

The presence of 10%, 30% and 50% methanol yields a well-defined wave with $E_{1/2} = -0.600$, -0.614 and -0.614 V *vs.* SCE respectively, $E_{1/2}$ is -0.6025 V for indium(III) in aqueous solution. This rules out complexation between the metal ions and methanol. A negative shift in $E_{1/2}$ on addition of increasing amounts of TDPA indicates complex formation.

The overall stability constants are summarized in Table I. Increasing the methanol concentration considerably increases the stability constants.

TABLE I.—STABILITY CONSTANTS FOR In(III)-TDPA SYSTEM

Methanol conc. of the media %	β_1	β_2	β_3	β_4
0	20	80	2.4×10^2	2.6×10^3
10	31	80	2.6×10^2	2.8×10^3
30	44	2.1×10^2	4.3×10^2	3.4×10^3
50	120	3.0×10^2	12.0×10^2	17.8×10^3

Uranyl–TDPA System

Uranyl ion in TDPA gives a diffusion-controlled reversible one-electron reduction at the DME in aqueous and 30% methanol media.

A negative shift in $E_{1/2}$ coupled with a decrease in diffusion current with increasing concentration of TDPA indicates complexation. The values for β_1, β_2 and β_3 are 3.3, 1.2 and 8.5 in aqueous media; in 30% methanolic media the corresponding values are 5.5, 1.2 and 34. Again addition of methanol increases the stability.

Acknowledgement—We thank Prof. R. C. Mehrotra, University of Rajasthan, Jaipur and Prof. R. M. Advani of M.R.E. College, Jaipur for their interest and provision of research facilities.

Department of Chemistry
M.R.E. College
Jaipur-4, India
P. C. RAWAT

Chemical Laboratories
University of Rajasthan
Jaipur-4, India
C. M. GUPTA

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water–methanol solutions at 30 ± 0·1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in 0·1*M* HCl, with 0·1*M* KCl as supporting electrolyte.

Zusammenfassung—Die Komplexbildung von In(III) und U(VI) mit Thiodipropionsäure wurde polarographisch in Wasser und Wasser-Methanol bei 30 ± 0,1° untersucht. Alle Chelate gehören zu polarographisch reversiblen Systemen. Mit Indium(III) werden bei pH 4,8 Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2, 1:3 und 1:4 gefunden. Uran(VI) bildet in 0,01 M HCl mit 0,1 M KCl als Leitelektrolyt nacheinander drei Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2 und 1:3.

Résumé—On a étudié polarographiquement la complexation de In(III) et U(VI) avec l'acide thiodipropionique en solution dans l'eau et l'eauméthanol à 30 ± 0,1°. Tous les chélates appartiennent à des systèmes réversibles polarographiquement. Avec l'indium(III), on trouve des complexes avec des rapports métal:ligand de 1:1, 1:2, 1:3 et 1:4 à pH 4,8. On trouve que l'uranium(VI) forme trois complexes successifs avec des rapports métal:ligand de 1:1, 1:2 et 1:3 en HCl 0,01*M* avec KCl 0,1*M* comme électrolyte support.

REFERENCES

1. P. C. Rawat and C. M. Gupta, *J. Inorg. Nucl. Chem.*, 1972, **34**, 951.
2. *Idem*, *ibid.*, 1972, **34**, 1621.
3. D. D. Deford, D. N. Hume, *J. Am. Chem. Soc.*, 1951, **73**, 5321.
4. H. Irving, *Advan. Polarog.*, 1960, **1**, 42.

Talanta, 1972, Vol. 19, pp. 708 to 711. Pergamon Press. Printed in Northern Ireland

Determination of $\mathrm{p}K_a$ of acetic and benzoic acids in pyridine

(*Received* 23 *June* 1971. *Accepted* 2 *October* 1971)

FROM AN ANALYSIS of half-neutralization potentials (HNP) in pyridine referred to that of benzoic acid, Streuli and Miron[1] were able to classify a number of organic acids, including certain aliphatic

Uranyl-TDPA System

Uranyl ion in TDPA gives a diffusion-controlled reversible one-electron reduction at the DME in aqueous and 30% methanol media.

A negative shift in $E_{1/2}$ coupled with a decrease in diffusion current with increasing concentration of TDPA indicates complexation. The values for β_1, β_2 and β_3 are 3.3, 1.2 and 8.5 in aqueous media; in 30% methanolic media the corresponding values are 5.5, 1.2 and 34. Again addition of methanol increases the stability.

Acknowledgement—We thank Prof. R. C. Mehrotra, University of Rajasthan, Jaipur and Prof. R. M. Advani of M.R.E. College, Jaipur for their interest and provision of research facilities.

Department of Chemistry
M.R.E. College
Jaipur-4, India
P. C. RAWAT

Chemical Laboratories
University of Rajasthan
Jaipur-4, India
C. M. GUPTA

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water–methanol solutions at 30 ± 0·1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in 0·1*M* HCl, with 0·1*M* KCl as supporting electrolyte.

Zusammenfassung—Die Komplexbildung von In(III) und U(VI) mit Thiodipropionsäure wurde polarographisch in Wasser und Wasser-Methanol bei 30 ± 0,1° untersucht. Alle Chelate gehören zu polarographisch reversiblen Systemen. Mit Indium(III) werden bei pH 4,8 Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2, 1:3 und 1:4 gefunden. Uran(VI) bildet in 0,01 M HCl mit 0,1 M KCl als Leitelektrolyt nacheinander drei Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2 und 1:3.

Résumé—On a étudié polarographiquement la complexation de In(III) et U(VI) avec l'acide thiodipropionique en solution dans l'eau et l'eauméthanol à 30 ± 0,1°. Tous les chélates appartiennent à des systèmes réversibles polarographiquement. Avec l'indium(III), on trouve des complexes avec des rapports métal:ligand de 1:1, 1:2, 1:3 et 1:4 à pH 4,8. On trouve que l'uranium(VI) forme trois complexes successifs avec des rapports métal:ligand de 1:1, 1:2 et 1:3 en HCl 0,01*M* avec KCl 0,1*M* comme électrolyte support.

REFERENCES

1. P. C. Rawat and C. M. Gupta, *J. Inorg. Nucl. Chem.*, 1972, **34**, 951.
2. *Idem, ibid.*, 1972, **34**, 1621.
3. D. D. Deford, D. N. Hume, *J. Am. Chem. Soc.*, 1951, **73**, 5321.
4. H. Irving, *Advan. Polarog.*, 1960, **1**, 42.

Talanta, 1972, Vol. 19, pp. 708 to 711. Pergamon Press. Printed in Northern Ireland

Determination of pK_a of acetic and benzoic acids in pyridine

(*Received* 23 *June* 1971. *Accepted* 2 *October* 1971)

FROM AN ANALYSIS of half-neutralization potentials (HNP) in pyridine referred to that of benzoic acid, Streuli and Miron[1] were able to classify a number of organic acids, including certain aliphatic

and aromatic mono- and dicarboxylic acids and phenols. The characteristic linear dependence of ΔHNP *vs*. $\mathrm{p}K_a^{aq}$ was broadly used in comparing the relative acidities of different groups of acids and in formulating criteria for their resolution. Although it is possible to obtain some estimates of *relative* $\mathrm{p}K_a$ values from these generalizations, unfortunately no information on the absolute $\mathrm{p}K_a$ of any of the acids can be derived. Subsequently, Elving and co-workers[2] noticed that nitric acid ($\mathrm{p}K_a^{aq} = -1{\cdot}3$) falls on the same smooth curve obtained on plotting the polarographic half-wave potentials ($E_{1/2}$) of hydrogen ion reduction in pyridine solutions of several monocarboxylic acids (using tetraethylammonium perchlorate as the supporting electrolyte) as a function of their $\mathrm{p}K_a^{aq}$ values. If it is assumed that acids of the same charge type maintain the same relative relationship in both water and pyridine, 10·09 and 9·56 are obtained as the estimated $\mathrm{p}K_a$ values for acetic and benzoic acid on the basis of the known value (4·06)[3] of the $\mathrm{p}K_a$ of nitric acid in pyridine. These estimates do indeed seem to agree with the earlier notion[4,5] that the carboxylic acids, in general, are extremely weakly dissociated in pyridine. The purpose of the present work was to determine the overall dissociation constant of acetic and benzoic acid in pyridine by conventional methods. Our preliminary attempts,[6] in this connection, involving the use of the $\mathrm{Pt/H_2}$ electrode in solutions of relatively large concentrations of the organic acid in the presence of nitric acid are considered unsatisfactory. In this investigation we chose to use "buffer" solutions composed of tetrabutylammonium salts and the acids in question. The work consisted of differential vapour pressure (DVP) studies of solutions of the acids and the salts, and of the acid/salt mixtures, as well as measurement of hydrogen ion activities of the latter (with a glass electrode).

Although the DVP measurements on tetrabutylammonium acetate and benzoate are considered helpful in providing independent estimates of the dissociation constants of these electrolytes, their precision is relatively low; furthermore, the temperature (37°) at which they had to be made prevents direct correlation of the results with those generally obtained at 25°. Because of these limitations, it was considered expedient to use the conductometric values of the salt dissociation constants obtained at 25° in the final calculations. The dissociation constant of tetrabutylammonium acetate in pyridine is already available[7]; however, since no such estimate for tetrabutylammonium benzoate has yet been reported, additional studies on this system have also been undertaken.

The experimental techniques and treatment of data are essentially the same as those described in our earlier work.[3,8,9,10] A Beckman glass electrode (#39099E-3) was used against an $\mathrm{Hg/HgCl_{2(s)}}$, $\mathrm{LiCl_{(s)}}$ reference; the electrode was calibrated with solutions of nitric acid in pyridine, of known $\mathrm{H^+}$-activity. For the DVP results, the Marshall-Grunwald equation[11] was used to evaluate the ionic activity coefficients.

RESULTS AND DISCUSSION

Differential vapour pressure measurements at 37° showed that solutions of the two acids closely resemble solutions of the standard monomer 1,3-diphenylguanidine in their behaviour, indicating that these two acids exist primarily as monomers in pyridine. On the other hand, the salts tetrabutylammonium acetate and benzoate are evidently slightly dissociated; the average dissociation constants are calculated[3] to be $2{\cdot}04 \times 10^{-4}$ and $1{\cdot}99 \times 10^{-4}$ respectively. The tetrabutylammonium acetate value is close to that ($1{\cdot}7 \times 10^{-4}$) reported[7] from conductance measurements at 25°.

TABLE I.—RESULTS OF DIFFERENTIAL VAPOUR PRESSURE STUDIES OF ACID–SALT MIXTURES

Acetic acid, *M*	Tetrabutyl-ammonium acetate, *M*	ΔT		Benzoic acid, *M*	Tetrabutyl-ammonium benzoate, *M*	ΔT	
		Obsd.*	Calcd.†			Obsd.*	Calcd.†
0·0320	0·0458	$17{\cdot}4_6$	17·4	$0{\cdot}0262_5$	$0{\cdot}0183_5$	$10{\cdot}2_4$	10·2
0·0513	0·0183	$14{\cdot}6_5$	14·9	0·0292	0·0197	$10{\cdot}1_4$	11·5
0·0534	0·0153	$14{\cdot}2_8$	14·7	0·0401	$0{\cdot}0162_5$	$11{\cdot}9_8$	13·0
0·0257	0·0549	$17{\cdot}8_5$	18·2	0·0336	0·0150	$10{\cdot}6_2$	11·2

* Average of 4 or 5 readings

† Sum of individual values for the acid and the salt.

The results for acid-salt mixtures are presented in Table I. The additivity of the individual ΔT values suggests that the acid molecules are extremely weakly dissociated and exist virtually as monomers. It also indicates the absence of any other interaction(s) that would cause change in the overall molarity.

From the conductance measurements at 25° on tetrabutylammonium benzoate, presented as a plot

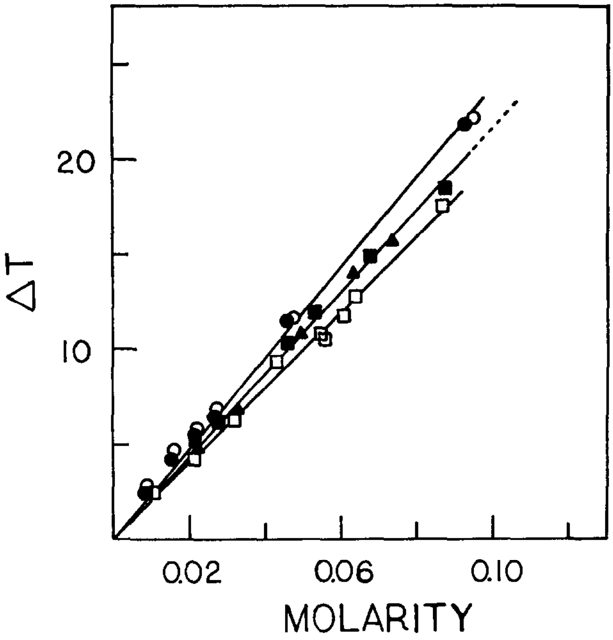


FIG. 1.—Differential vapour pressure measurements at 37°C. ▲-1,3-diphenylguanidine ☐-Acetic acid ■-Benzoic acid ○-Tetrabutylammonium acetate ●-Tetrabutylammonium benzoate. Average lines shown in the figure.

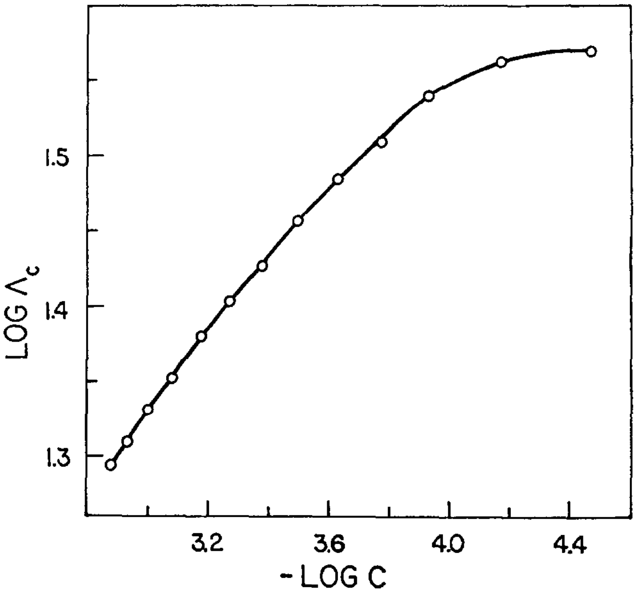


FIG. 2.—Conductance measurements on tetrabutylammonium benzoate at 25°.

of log Λ_0 *vs.* $-\log C$, a value of 2·00 × 10^{-4} was obtained for the dissociation constant of this salt (Fig. 2). (The close agreement with the DVP value at 37° suggests that the dissociation constant is practically independent of temperature.) The limiting conductance is found to be 44·6 $\text{ohm}^{-1}.\text{cm}^{-1}.\text{equiv}^{-1}$. Since the λ° of $(\text{n-C}_4\text{H}_9)_4\text{N}^+$ is 24·0,[7] the limiting conductance of benzoate ion is calculated to be 20.6—a value comparable to the limiting conductance of $\text{FB(C}_6\text{H}_5)_3^-$ in this solvent (24·0)[7].

TABLE II.—RESULTS OF GLASS ELECTRODE MEASUREMENTS ON ACID–SALT MIXTURES

Acetic acid, *M*	Tetrabutyl-ammonium acetate, *M*	$a_{\text{H}^+} \times 10^9$	pK_a of acetic acid*	Benzoic acid, *M*	Tetrabutyl-ammonium benzoate, *M*	$a_{\text{H}^+} \times 10^8$	pK_a of Benzoic acid*
0·1172	0·00149	7·586	10·49	0·1051	0·00218	1·772	9·95
0·1622	0·00138	22·39	10·18	0·1089		1·922	9·93
0·2343	0·00119	39·81	10·12	0·1216		2·152	9·93
0·3515	$0{\cdot}00089_5$	154·9	9·77	0·1536		3·709	9·80
			Av. $10{\cdot}1_4$	0·1640		4·185	9·77
				0·2316		8·433	9·62
				0·2441		9·440	9·59
							Av. $9{\cdot}8_0$

* Calculated from $K_a = a_{\text{H}^+}\sqrt{K_{\text{MX}}\,C_{\text{MX}}}/C_{\text{HX}}$ where $K_{\text{MX}} = a_{\text{M}^+}a_{\text{X}^-}/[\text{MX}]$; C_{HX} and C_{MX} are the analytical concentrations of HX and MX.

The results of experiments with the glass electrode are presented in Table II. Calculations yield 10·1 and 9·8 for the average values of pK_a for acetic and benzoic acid, respectively, as compared to the values 4·73 and 4·20 in water, indicating that both acids are indeed very weakly dissociated in pyridine. Also it is interesting to note that the two acids do maintain almost the same relative pK_a relationship[1] (ΔpK_a = 0·3 in pyridine *vs.* 0·53 in water) in pyridine and water.

Chemistry Department
Illinois State University
Normal, Ill. 61761 *U.S.A.*

L. M. MUKHERJEE*
RONALD S. SCHULTZ

Summary—The pK_a's of acetic acid and benzoic acid in pyridine as solvent are found to be 10·1 and 9·8, respectively, at 25°. These results are based on measurements of hydrogen ion activities in mixtures of the acids and their tetrabutylammonium salts. Supplementary studies of differential vapour pressure characteristics of solutions of the acids and the acid–salt mixtures, and conductance of tetrabutylammonium benzoate solutions are also incorporated.

Zusammenfassung—Die pK_a-Werte von Eissigsäure und Benzoesäure in Pyridin als Lösungsmittel betragen bei 25° 10,1 bzw. 9,8. Diese Ergebnisse stützen sich auf Messungen von Wasserstoffionenaktivitäten in Gemischen der Säuren mit ihren Tetrabutylammoniumsalzen. Darüber hinaus werden die Differential-Dampfdruckeigenschaften von Lösungen der Säuren und der Säure-Salz-Gemische sowie die Leitfähigkeit von Tetrabutylammoniumbenzoat-Lösungen mitgeteilt.

Résumé—On a trouvé que les valeurs des pK_a de l'acide acétique et de l'acide benzoïque en pyridine sont respectivement de 10,1 et 9,8 à 25°. Ces résultats sont basés sur des mesures d'activités d'ion hydrogène dans des mélanges des acides et de leurs sels de tétrabutylammonium. On a aussi incorporé des études complémentaires de caractéristiques de pression de vapeur différentielle de solutions des acides et des mélanges acide-sel, et de conductance de solutions de benzoate de tétrabutylammonium.

---

* Address all correspondence to this author c/o School of Chemistry, University of Minnesota, Minneapolis, Minn. 55455., U.S.A.

REFERENCES

1. C. A. Streuli and R. R. Miron, *Anal. Chem.*, 1958, **30**, 1978.
2. K. Tsuji and P. J. Elving, *ibid.*, 1969, **41**, 286.
3. L. M. Mukherjee, J. J. Kelly, W. Baranetzky and J. Sica, *J. Phys. Chem.*, 1968, **72**, 3410.
4. A. Hantzsch and K. S. Caldwell, *Z. Phys. Chem.*, 1908, **61**, 227.
5. M. M. Davies, *Trans. Faraday Soc.*, 1935, **31**, 1561.
6. J. J. Kelly, *M. S. Thesis*, Polytechnic Institute of Brooklyn, Brooklyn, New York, 1967.
7. D. S. Burgess and C. A. Kraus, *J. Am. Chem. Soc.*, 1948, **70**, 706.
8. L. M. Mukherjee and J. M. Lukacs, Jr., *J. Phys. Chem.*, 1969, **73**, 3115.
9. L. M. Mukherjee *ibid.*, (in the press).
10. L. M. Mukherjee, J. J. Kelly, M. Richards and J. M. Lukacs, Jr., *ibid.*, 1969, **73**, 580.
11. H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, 1953, **21**, 2143.

Talanta, 1972, Vol. 19, pp. 711 to 713. Pergamon Press. Printed in Northern Ireland

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions

(*Received* 13 *August* 1971. *Accepted* 17 *November* 1971)

THIS COMMUNICATION gives the results of the determination of the stability constants of the Mn(II), Ni, Zn and Cu(II) chelates of five closely related *N*-arylhydroxamic acids by pH titration.[1]

EXPERIMENTAL

Hydroxamic acids (*Table I*). Synthesized by the method of Priyadarshini and Tandon,[1] recrystallized from a mixture of benzene and petroleum ether, and dried in vacuum over phosphorus pentoxide. Purity was confirmed by elemental analyses, m.p., and spectroscopy.

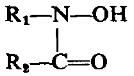
Procedure. As described earlier.[2]

RESULTS

The results were calculated as in previous work,[2] and are given in Table II. The chelates of Mn(II), Ni, and Zn with *m*-TBHA and *p*-TBHA were so insoluble that they separated out immediately on

TABLE I.—DETAILS OF HYDROXAMIC ACIDS

General formula



$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\;\; | \\ R_2\text{—C=O} \end{array}$$

Hydroxamic acid	Trivial name	R_1	R_2	Melting point,* °C
N-Phenylbenzo-	PBHA	C_6H_5—	C_6H_5—	121 (121)[8]
N-*o*-Tolylbenzo-	*o*-TBHA	*o*-$CH_3\cdot C_6H_4$—	C_6H_5—	109 (108)[9]
N-*m*-Tolylbenzo-	*m*-TBHA	*m*-$CH_3\cdot C_6H_4$—	C_6H_5—	68 (67)[9]
N-*p*-Tolylbenzo-	*p*-TBHA	*p*-$CH_3\cdot C_6H_4$—	C_6H_5—	112 (111)[8]
N-Phenyl-n-butyro-	P(n)BHA	C_6H_5—	CH_3-$(CH_2)_2$—	81 (81)[1]

* Reported values in brackets.

Uranyl–TDPA System

Uranyl ion in TDPA gives a diffusion-controlled reversible one-electron reduction at the DME in aqueous and 30% methanol media.

A negative shift in $E_{1/2}$ coupled with a decrease in diffusion current with increasing concentration of TDPA indicates complexation. The values for β_1, β_2 and β_3 are 3.3, 1.2 and 8.5 in aqueous media; in 30% methanolic media the corresponding values are 5.5, 1.2 and 34. Again addition of methanol increases the stability.

Acknowledgement—We thank Prof. R. C. Mehrotra, University of Rajasthan, Jaipur and Prof. R. M. Advani of M.R.E. College, Jaipur for their interest and provision of research facilities.

Department of Chemistry
M.R.E. College
Jaipur-4, India
P. C. RAWAT

Chemical Laboratories
University of Rajasthan
Jaipur-4, India
C. M. GUPTA

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water–methanol solutions at 30 ± 0·1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in 0·1*M* HCl, with 0·1*M* KCl as supporting electrolyte.

Zusammenfassung—Die Komplexbildung von In(III) und U(VI) mit Thiodipropionsäure wurde polarographisch in Wasser und Wasser-Methanol bei 30 ± 0,1° untersucht. Alle Chelate gehören zu polarographisch reversiblen Systemen. Mit Indium(III) werden bei pH 4,8 Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2, 1:3 und 1:4 gefunden. Uran(VI) bildet in 0,01 M HCl mit 0,1 M KCl als Leitelektrolyt nacheinander drei Komplexe mit den Metall:Ligand-Verhältnissen 1:1, 1:2 und 1:3.

Résumé—On a étudié polarographiquement la complexation de In(III) et U(VI) avec l'acide thiodipropionique en solution dans l'eau et l'eauméthanol à 30 ± 0,1°. Tous les chélates appartiennent à des systèmes réversibles polarographiquement. Avec l'indium(III), on trouve des complexes avec des rapports métal:ligand de 1:1, 1:2, 1:3 et 1:4 à pH 4,8. On trouve que l'uranium(VI) forme trois complexes successifs avec des rapports métal:ligand de 1:1, 1:2 et 1:3 en HCl 0,01*M* avec KCl 0,1*M* comme électrolyte support.

REFERENCES

1. P. C. Rawat and C. M. Gupta, *J. Inorg. Nucl. Chem.*, 1972, **34**, 951.
2. *Idem*, *ibid.*, 1972, **34**, 1621.
3. D. D. Deford, D. N. Hume, *J. Am. Chem. Soc.*, 1951, **73**, 5321.
4. H. Irving, *Advan. Polarog.*, 1960, **1**, 42.

Talanta, 1972, Vol. 19, pp. 708 to 711. Pergamon Press. Printed in Northern Ireland

Determination of pK_a of acetic and benzoic acids in pyridine

(*Received* 23 *June* 1971. *Accepted* 2 *October* 1971)

FROM AN ANALYSIS of half-neutralization potentials (HNP) in pyridine referred to that of benzoic acid, Streuli and Miron[1] were able to classify a number of organic acids, including certain aliphatic

and aromatic mono- and dicarboxylic acids and phenols. The characteristic linear dependence of ΔHNP *vs.* pK_a^{aq} was broadly used in comparing the relative acidities of different groups of acids and in formulating criteria for their resolution. Although it is possible to obtain some estimates of *relative* pK_a values from these generalizations, unfortunately no information on the absolute pK_a of any of the acids can be derived. Subsequently, Elving and co-workers[2] noticed that nitric acid ($pK_a^{aq} = -1{\cdot}3$) falls on the same smooth curve obtained on plotting the polarographic half-wave potentials ($E_{1/2}$) of hydrogen ion reduction in pyridine solutions of several monocarboxylic acids (using tetraethylammonium perchlorate as the supporting electrolyte) as a function of their pK_a^{aq} values. If it is assumed that acids of the same charge type maintain the same relative relationship in both water and pyridine, 10·09 and 9·56 are obtained as the estimated pK_a values for acetic and benzoic acid on the basis of the known value (4·06)[3] of the pK_a of nitric acid in pyridine. These estimates do indeed seem to agree with the earlier notion[4,5] that the carboxylic acids, in general, are extremely weakly dissociated in pyridine. The purpose of the present work was to determine the overall dissociation constant of acetic and benzoic acid in pyridine by conventional methods. Our preliminary attempts,[6] in this connection, involving the use of the Pt/H_2 electrode in solutions of relatively large concentrations of the organic acid in the presence of nitric acid are considered unsatisfactory. In this investigation we chose to use "buffer" solutions composed of tetrabutylammonium salts and the acids in question. The work consisted of differential vapour pressure (DVP) studies of solutions of the acids and the salts, and of the acid/salt mixtures, as well as measurement of hydrogen ion activities of the latter (with a glass electrode).

Although the DVP measurements on tetrabutylammonium acetate and benzoate are considered helpful in providing independent estimates of the dissociation constants of these electrolytes, their precision is relatively low; furthermore, the temperature (37°) at which they had to be made prevents direct correlation of the results with those generally obtained at 25°. Because of these limitations, it was considered expedient to use the conductometric values of the salt dissociation constants obtained at 25° in the final calculations. The dissociation constant of tetrabutylammonium acetate in pyridine is already available[7]; however, since no such estimate for tetrabutylammonium benzoate has yet been reported, additional studies on this system have also been undertaken.

The experimental techniques and treatment of data are essentially the same as those described in our earlier work.[3,8,9,10] A Beckman glass electrode (#39099E-3) was used against an $Hg/HgCl_{2(s)}$, $LiCl_{(s)}$ reference; the electrode was calibrated with solutions of nitric acid in pyridine, of known H^+-activity. For the DVP results, the Marshall-Grunwald equation[11] was used to evaluate the ionic activity coefficients.

RESULTS AND DISCUSSION

Differential vapour pressure measurements at 37° showed that solutions of the two acids closely resemble solutions of the standard monomer 1,3-diphenylguanidine in their behaviour, indicating that these two acids exist primarily as monomers in pyridine. On the other hand, the salts tetrabutylammonium acetate and benzoate are evidently slightly dissociated; the average dissociation constants are calculated[3] to be $2{\cdot}04 \times 10^{-4}$ and $1{\cdot}99 \times 10^{-4}$ respectively. The tetrabutylammonium acetate value is close to that ($1{\cdot}7 \times 10^{-4}$) reported[7] from conductance measurements at 25°.

TABLE I.—RESULTS OF DIFFERENTIAL VAPOUR PRESSURE STUDIES OF ACID–SALT MIXTURES

Acetic acid, *M*	Tetrabutyl-ammonium acetate, *M*	ΔT		Benzoic acid, *M*	Tetrabutyl-ammonium benzoate, *M*	ΔT	
		Obsd.*	Calcd.†			Obsd.*	Calcd.†
0·0320	0·0458	$17{\cdot}4_6$	17·4	$0{\cdot}0262_5$	$0{\cdot}0183_5$	$10{\cdot}2_4$	10·2
0·0513	0·0183	$14{\cdot}6_5$	14·9	0·0292	0·0197	$10{\cdot}1_4$	11·5
0·0534	0·0153	$14{\cdot}2_8$	14·7	0·0401	$0{\cdot}0162_5$	$11{\cdot}9_8$	13·0
0·0257	0·0549	$17{\cdot}8_5$	18·2	0·0336	0·0150	$10{\cdot}6_2$	11·2

* Average of 4 or 5 readings

† Sum of individual values for the acid and the salt.

The results for acid-salt mixtures are presented in Table I. The additivity of the individual ΔT values suggests that the acid molecules are extremely weakly dissociated and exist virtually as monomers. It also indicates the absence of any other interaction(s) that would cause change in the overall molarity.

From the conductance measurements at 25° on tetrabutylammonium benzoate, presented as a plot

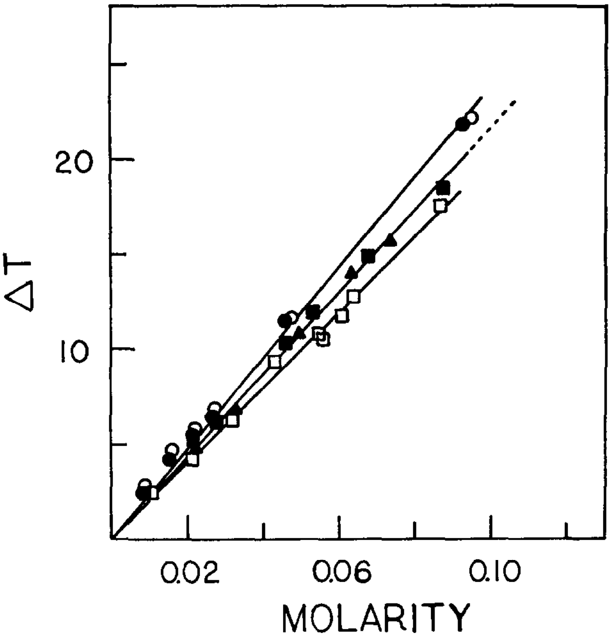


FIG. 1.—Differential vapour pressure measurements at 37°C. ▲-1,3-diphenylguanidine □-Acetic acid ■-Benzoic acid ○-Tetrabutylammonium acetate ●-Tetrabutylammonium benzoate. Average lines shown in the figure.

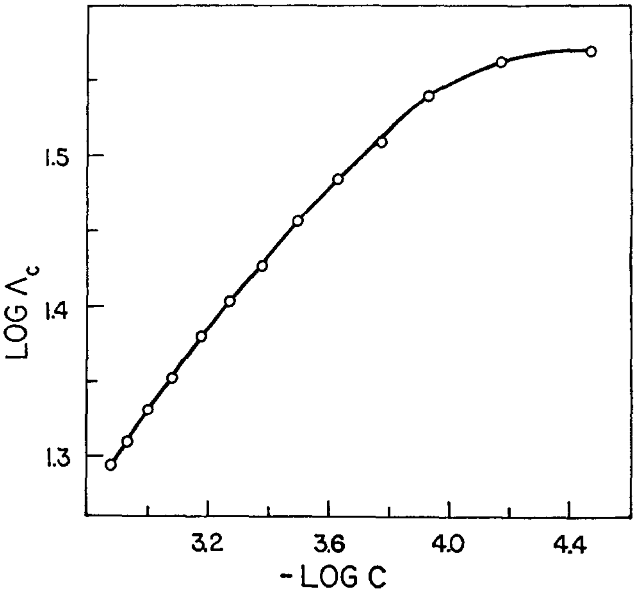


FIG. 2.—Conductance measurements on tetrabutylammonium benzoate at 25°.

of log Λ_0 *vs.* $-\log C$, a value of $2{\cdot}00 \times 10^{-4}$ was obtained for the dissociation constant of this salt (Fig. 2). (The close agreement with the DVP value at 37° suggests that the dissociation constant is practically independent of temperature.) The limiting conductance is found to be 44·6 ohm^{-1}.cm^{-1}.equiv^{-1}. Since the λ° of $(n\text{-}C_4H_9)_4N^+$ is 24·0,[7] the limiting conductance of benzoate ion is calculated to be 20.6—a value comparable to the limiting conductance of $FB(C_6H_5)_3^-$ in this solvent (24·0)[7].

TABLE II.—RESULTS OF GLASS ELECTRODE MEASUREMENTS ON ACID–SALT MIXTURES

Acetic acid, M	Tetrabutylammonium acetate, M	$a_{H^+} \times 10^9$	pK_a of acetic acid*	Benzoic acid, M	Tetrabutylammonium benzoate, M	$a_{H^+} \times 10^8$	pK_a of Benzoic acid*
0·1172	0·00149	7·586	10·49	0·1051	0·00218	1·772	9·95
0·1622	0·00138	22·39	10·18	0·1089		1·922	9·93
0·2343	0·00119	39·81	10·12	0·1216		2·152	9·93
0·3515	$0{\cdot}00089_5$	154·9	9·77	0·1536		3·709	9·80
			Av. $10{\cdot}1_4$	0·1640		4·185	9·77
				0·2316		8·433	9·62
				0·2441		9·440	9·59
							Av. $9{\cdot}8_0$

* Calculated from $K_a = a_{H^+}\sqrt{K_{MX}\,C_{MX}}/C_{HX}$ where $K_{MX} = a_{M^+}a_{X^-}/[MX]$; C_{HX} and C_{MX} are the analytical concentrations of HX and MX.

The results of experiments with the glass electrode are presented in Table II. Calculations yield 10·1 and 9·8 for the average values of pK_a for acetic and benzoic acid, respectively, as compared to the values 4·73 and 4·20 in water, indicating that both acids are indeed very weakly dissociated in pyridine. Also it is interesting to note that the two acids do maintain almost the same relative pK_a relationship[1] (ΔpK_a = 0·3 in pyridine *vs.* 0·53 in water) in pyridine and water.

Chemistry Department
Illinois State University
Normal, Ill. 61761 *U.S.A.*

L. M. MUKHERJEE*
RONALD S. SCHULTZ

Summary—The pK_a's of acetic acid and benzoic acid in pyridine as solvent are found to be 10·1 and 9·8, respectively, at 25°. These results are based on measurements of hydrogen ion activities in mixtures of the acids and their tetrabutylammonium salts. Supplementary studies of differential vapour pressure characteristics of solutions of the acids and the acid–salt mixtures, and conductance of tetrabutylammonium benzoate solutions are also incorporated.

Zusammenfassung—Die pK_a-Werte von Eissigsäure und Benzoesäure in Pyridin als Lösungsmittel betragen bei 25° 10,1 bzw. 9,8. Diese Ergebnisse stützen sich auf Messungen von Wasserstoffionenaktivitäten in Gemischen der Säuren mit ihren Tetrabutylammoniumsalzen. Darüber hinaus werden die Differential-Dampfdruckeigenschaften von Lösungen der Säuren und der Säure-Salz-Gemische sowie die Leitfähigkeit von Tetrabutylammoniumbenzoat-Lösungen mitgeteilt.

Résumé—On a trouvé que les valeurs des pK_a de l'acide acétique et de l'acide benzoïque en pyridine sont respectivement de 10,1 et 9,8 à 25°. Ces résultats sont basés sur des mesures d'activités d'ion hydrogène dans des mélanges des acides et de leurs sels de tétrabutylammonium. On a aussi incorporé des études complémentaires de caractéristiques de pression de vapeur différentielle de solutions des acides et des mélanges acide-sel, et de conductance de solutions de benzoate de tétrabutylammonium.

---

* Address all correspondence to this author c/o School of Chemistry, University of Minnesota, Minneapolis, Minn. 55455., U.S.A.

REFERENCES

1. C. A. Streuli and R. R. Miron, *Anal. Chem.*, 1958, **30**, 1978.
2. K. Tsuji and P. J. Elving, *ibid.*, 1969, **41**, 286.
3. L. M. Mukherjee, J. J. Kelly, W. Baranetzky and J. Sica, *J. Phys. Chem.*, 1968, **72**, 3410.
4. A. Hantzsch and K. S. Caldwell, *Z. Phys. Chem.*, 1908, **61**, 227.
5. M. M. Davies, *Trans. Faraday Soc.*, 1935, **31**, 1561.
6. J. J. Kelly, *M. S. Thesis*, Polytechnic Institute of Brooklyn, Brooklyn, New York, 1967.
7. D. S. Burgess and C. A. Kraus, *J. Am. Chem. Soc.*, 1948, **70**, 706.
8. L. M. Mukherjee and J. M. Lukacs, Jr., *J. Phys. Chem.*, 1969, **73**, 3115.
9. L. M. Mukherjee *ibid.*, (in the press).
10. L. M. Mukherjee, J. J. Kelly, M. Richards and J. M. Lukacs, Jr., *ibid.*, 1969, **73**, 580.
11. H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, 1953, **21**, 2143.

Talanta, 1972, Vol. 19, pp. 711 to 713. Pergamon Press. Printed in Northern Ireland

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions

(*Received* 13 *August* 1971. *Accepted* 17 *November* 1971)

THIS COMMUNICATION gives the results of the determination of the stability constants of the Mn(II), Ni, Zn and Cu(II) chelates of five closely related *N*-arylhydroxamic acids by pH titration.[1]

EXPERIMENTAL

Hydroxamic acids (*Table I*). Synthesized by the method of Priyadarshini and Tandon,[1] recrystallized from a mixture of benzene and petroleum ether, and dried in vacuum over phosphorus pentoxide. Purity was confirmed by elemental analyses, m.p., and spectroscopy.

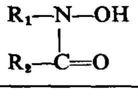
Procedure. As described earlier.[2]

RESULTS

The results were calculated as in previous work,[2] and are given in Table II. The chelates of Mn(II), Ni, and Zn with *m*-TBHA and *p*-TBHA were so insoluble that they separated out immediately on

TABLE I.—DETAILS OF HYDROXAMIC ACIDS

General formula



$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\;\; | \\ R_2\text{—C=O} \end{array}$$

Hydroxamic acid	Trivial name	R_1	R_2	Melting point,* °C
N-Phenylbenzo-	PBHA	C_6H_5—	C_6H_5—	121 (121)[8]
N-*o*-Tolylbenzo-	*o*-TBHA	*o*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	109 (108)[9]
N-*m*-Tolylbenzo-	*m*-TBHA	*m*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	68 (67)[9]
N-*p*-Tolylbenzo-	*p*-TBHA	*p*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	112 (111)[8]
N-Phenyl-n-butyro-	P(n)BHA	C_6H_5—	CH_3-$(CH_2)_2$—	81 (81)[1]

---

* Reported values in brackets.

REFERENCES

1. C. A. Streuli and R. R. Miron, *Anal. Chem.*, 1958, **30**, 1978.
2. K. Tsuji and P. J. Elving, *ibid.*, 1969, **41**, 286.
3. L. M. Mukherjee, J. J. Kelly, W. Baranetzky and J. Sica, *J. Phys. Chem.*, 1968, **72**, 3410.
4. A. Hantzsch and K. S. Caldwell, *Z. Phys. Chem.*, 1908, **61**, 227.
5. M. M. Davies, *Trans. Faraday Soc.*, 1935, **31**, 1561.
6. J. J. Kelly, *M. S. Thesis*, Polytechnic Institute of Brooklyn, Brooklyn, New York, 1967.
7. D. S. Burgess and C. A. Kraus, *J. Am. Chem. Soc.*, 1948, **70**, 706.
8. L. M. Mukherjee and J. M. Lukacs, Jr., *J. Phys. Chem.*, 1969, **73**, 3115.
9. L. M. Mukherjee *ibid.*, (in the press).
10. L. M. Mukherjee, J. J. Kelly, M. Richards and J. M. Lukacs, Jr., *ibid.*, 1969, **73**, 580.
11. H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, 1953, **21**, 2143.

Talanta, 1972, Vol. 19, pp. 711 to 713. Pergamon Press. Printed in Northern Ireland

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions

(*Received* 13 *August* 1971. *Accepted* 17 *November* 1971)

THIS COMMUNICATION gives the results of the determination of the stability constants of the Mn(II), Ni, Zn and Cu(II) chelates of five closely related *N*-arylhydroxamic acids by pH titration.[1]

EXPERIMENTAL

Hydroxamic acids (*Table I*). Synthesized by the method of Priyadarshini and Tandon,[1] recrystallized from a mixture of benzene and petroleum ether, and dried in vacuum over phosphorus pentoxide. Purity was confirmed by elemental analyses, m.p., and spectroscopy.

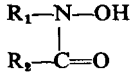
Procedure. As described earlier.[2]

RESULTS

The results were calculated as in previous work,[2] and are given in Table II. The chelates of Mn(II), Ni, and Zn with *m*-TBHA and *p*-TBHA were so insoluble that they separated out immediately on

TABLE I.—DETAILS OF HYDROXAMIC ACIDS

General formula



$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\;\; | \\ R_2\text{—C=O} \end{array}$$

Hydroxamic acid	Trivial name	R_1	R_2	Melting point,* °C
N-Phenylbenzo-	PBHA	C_6H_5—	C_6H_5—	121 (121)[8]
N-*o*-Tolylbenzo-	*o*-TBHA	*o*-$CH_3 \cdot C_6H_4$—	C_6H_5—	109 (108)[9]
N-*m*-Tolylbenzo-	*m*-TBHA	*m*-$CH_3 \cdot C_6H_4$—	C_6H_5—	68 (67)[9]
N-*p*-Tolylbenzo-	*p*-TBHA	*p*-$CH_3 \cdot C_6H_4$—	C_6H_5—	112 (111)[8]
N-Phenyl-n-butyro-	P(n)BHA	C_6H_5—	CH_3-$(CH_2)_2$—	81 (81)[1]

* Reported values in brackets.

TABLE II.—THERMODYNAMIC METAL–LIGAND STABILITY CONSTANTS AT 25°C

Complexing ion	Constant determined	Ligands				
		PBHA	*o*-TBHA	*m*-TBHA	*p*-TBHA	P(n)BHA
H^+	pK_a	11·04	11·12	11·12	11·13	11·45
Cu^{2+}	$\log K_1$	10·36	10·51	10·52	10·66	10·64
	$\log K_2$	8·78	8·85	8·86	8·79	8·87
	$\log (K_1/K_2)$	1·58	1·66	1·66	1·87	1·77
Zn^{2+}	$\log K_1$	7·51*	8·19	Ins.	Ins.	7·72
	$\log K_2$	6·63*	6·71			6·39
	$\log (K_1/K_2)$	0·88	1·48			1·33
Ni^{2+}	$\log K_1$	7·00*	7·64	Ins.	Ins.	7·61
	$\log K_2$	5·91*	6·06			5·69
	$\log (K_1/K_2)$	1·09	1·58			1·92
Mn^{2+}	$\log K_1$	6·02*	6·39	Ins.	Ins.	6·23
	$\log K_2$	5·15*	5·62			4·53
	$\log (K_1/K_2)$	0·87	0·77			1·70

Ins. = Insoluble.
* Calculated by Bjerrum-Calvin graphical method.
[Metal] 0·001*M*; [Ligand] 0·01*M*; [KOH] 0·1*M*.
Medium 50% (v/v) dioxan–water.

mixing the reagents or after addition of alkali. Attempts to determine their constants by decreasing the concentration of the metal ions to $5 \times 10^{-4}M$ did not succeed. In the acid range, Mn, Ni, and Zn complexes of PBHA gave maximum $\bar{n}$ values of 0·9. For such low values of $\bar{n}$, Goldberg's method[3] of calculation could not be applied and so the Bjerrum and Calvin graphical method was used. From the $\bar{n}$ values it appeared that precipitation started before formation of the 1:2 complex was complete. The stability constants were reproducible to 0·05 log units in replicate determinations, and variation of starting concentration of metal and ligand gave results varying by ±0·10 log units or less.

DISCUSSION

There was no evidence of metal ion hydrolysis, polynuclear complexes, protonated complexes, or influence of nitrate, chloride, perchlorate and alkali metal cations.

The Irving-Williams order of stabilities[4] was found to hold for all the systems with $K_1 > K_2$. The values of $\log K_1/K_2$ are consistently high for all copper complexes with a single exception. The $\Delta \log K$ value of 1·6–1·7 suggests that in these systems the electrostatic effect[5] has to be considered as well as the statistical effect (which gives $\log K = 0·6$).

Values of $\log K$ for copper are considerably higher than for the other metals and the values for Zn are greater than those for Ni. The higher value for the copper chelate may be due to a square planar structure. The order Zn > Ni has been observed earlier[6] and attributed to steric hindrance preventing the formation of a square planar Ni complex. Also the hydrolysis constant of Zn is greater than that of Ni, indicating greater affinity of Zn^{2+} for hydroxide ions; the NOH group of the hydroxamic acid resembles the OH group. These factors seem to account for the order Zn > Ni.

Since all the metal ions are bivalent and of much the same size, the electrostatic contribution to the metal–ligand bond in the first complexes formed with the same ligand is assumed to be very nearly the same. The $\log K_1$ values for the P(n)BHA, PBHA and *o*-TBHA complexes were a linear function of the overall ionization potentials of Mn(II), Zn(II) and Ni(II) but the points for the Cu(II) complexes were always above the line, confirming the higher stability of the copper complexes. The values of $\log K_1/K_2$ imply that there is little or no steric hindrance to the addition of the second chelate group. A plot of the stability constants for Cu(II) *vs.* the ligand protonation constants is linear, the equation being $\log K = 0·73\ pK_a + \text{constant}$. According to Jones and co-workers,[7] ligands with orbitals which can interact with suitable orbitals of the metal ion, give slopes greater than unity in such plots if the central ion has π-acceptor properties. They have further stated that Cu(II) and Ni(II) act as π-donors. The Cu(II) ion therefore seems to be acting as a π-donor.

The complexes of P(n)BHA with Zn, Ni and Mn(II) are less stable than the corresponding *o*-TBHA complexes, though P(n)BHA is more basic than *o*-TBHA. In contrast, the Cu(II) complexes follow the order of pK_a. Different geometries of the Cu and Zn, Ni and Mn complexes may be responsible for this unexpected behaviour in the stability order.

Acknowledgement—The authors are indebted to the authorities of Government Science Colleges, Jabalpur and Raipur for facilities. Grateful acknowledgement is made to the Chemical Society, London and van't Hoff fund, Amsterdam, for partial financial support. One of the authors (J. P. S.) is indebted to C.S.I.R., New Delhi for the award of a Junior Research Fellowhsip.

Department of Chemistry
Government College of Science
Raipur, M.P.
India

J. P. SHUKLA*
S. G. TANDON

Summary—Thermodynamic stability constants of complexes of Mn(II), Ni(II), Zn(II) and Cu(II) with five closely related *N*-arylhydroxamic acids have been determined at 25 ± 0·1° in 50% v/v aqueous dioxan medium. The stabilities of the complexes mostly follow the order of the basicity of the ligands and the electron affinities of the metal ions as measured by their second ionization potential.

Zusammenfassung—Die thermodynamischen Stabilitätskonstanten der Komplexe von Mn(II), Ni(II), Zn(II) und Cu(II) mit fünf nahe verwandte *N*-Arylhydroxamsäuren wurden bei 25 ± 0,1° in 50%(v/v) wäßrigem Dioxan gemessen. Die Stabilität der Komplexe schließt sich meistens an die Basizitätsreihenfolge der Liganden und an die Elektronenaffinitäten der Metallionen an, wie sie sich im zweiten Ionisierungspotential zeigen.

Résumé—On a déterminé les constantes de stabilité thermodynamique de complexes de Mn(II), Ni(II), Zn(II) et Cu(II) avec cinq acides *N*-arylhydroxamiques etroitement apparentés, à 25 ± 0,1° en milieu dioxane aqueux 50% v/v. Les stabilités des complexes suivent essentiellement l'ordre de basicité des ligands et les affinités électroniques des ions métalliques telles qu'elles sont mesurées par leur second potentiel d'ionisation.

REFERENCES

1. U. Priyadarshini and S. G. Tandon, *J. Chem. Eng. Data*, 1967, **12**, 143.
2. D. C. Bhura and S. G. Tandon, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2993.
3. D. E. Goldberg, *J. Chem. Educ.*, 1962, **39**, 328; 1963, **40**, 341.
4. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
5. N. Bjerrum, *Z. Physik. Chem.*, 1932, **106**, 238.
6. W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, 1954, **11**, 201, 301.
7. J. E. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 1958, 2001, 2010.
8. S. G. Tandon and S. C. Bhattacharya, *J. Chem. Eng. Data*, 1962, **7**, 553.
9. V. K. Gupta, *Proc. Indian Science Congress, Roorkee, India*, 1965–66.

* Present address: Radiochemistry Division, Bhadha Atomic Research Centre, Trombay, Bombay-85 (AS).

REFERENCES

1. C. A. Streuli and R. R. Miron, *Anal. Chem.*, 1958, **30**, 1978.
2. K. Tsuji and P. J. Elving, *ibid.*, 1969, **41**, 286.
3. L. M. Mukherjee, J. J. Kelly, W. Baranetzky and J. Sica, *J. Phys. Chem.*, 1968, **72**, 3410.
4. A. Hantzsch and K. S. Caldwell, *Z. Phys. Chem.*, 1908, **61**, 227.
5. M. M. Davies, *Trans. Faraday Soc.*, 1935, **31**, 1561.
6. J. J. Kelly, *M. S. Thesis*, Polytechnic Institute of Brooklyn, Brooklyn, New York, 1967.
7. D. S. Burgess and C. A. Kraus, *J. Am. Chem. Soc.*, 1948, **70**, 706.
8. L. M. Mukherjee and J. M. Lukacs, Jr., *J. Phys. Chem.*, 1969, **73**, 3115.
9. L. M. Mukherjee *ibid.*, (in the press).
10. L. M. Mukherjee, J. J. Kelly, M. Richards and J. M. Lukacs, Jr., *ibid.*, 1969, **73**, 580.
11. H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, 1953, **21**, 2143.

Talanta, 1972, Vol. 19, pp. 711 to 713. Pergamon Press. Printed in Northern Ireland

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions

(*Received* 13 *August* 1971. *Accepted* 17 *November* 1971)

THIS COMMUNICATION gives the results of the determination of the stability constants of the Mn(II), Ni, Zn and Cu(II) chelates of five closely related *N*-arylhydroxamic acids by pH titration.[1]

EXPERIMENTAL

Hydroxamic acids (*Table I*). Synthesized by the method of Priyadarshini and Tandon,[1] recrystallized from a mixture of benzene and petroleum ether, and dried in vacuum over phosphorus pentoxide. Purity was confirmed by elemental analyses, m.p., and spectroscopy.

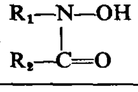
Procedure. As described earlier.[2]

RESULTS

The results were calculated as in previous work,[2] and are given in Table II. The chelates of Mn(II), Ni, and Zn with *m*-TBHA and *p*-TBHA were so insoluble that they separated out immediately on

TABLE I.—DETAILS OF HYDROXAMIC ACIDS

General formula



$$\begin{matrix} R_1\text{—N—OH} \\ | \\ R_2\text{—C=O} \end{matrix}$$

Hydroxamic acid	Trivial name	R_1	R_2	Melting point,* °C
N-Phenylbenzo-	PBHA	C_6H_5—	C_6H_5—	121 (121)[8]
N-*o*-Tolylbenzo-	*o*-TBHA	*o*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	109 (108)[9]
N-*m*-Tolylbenzo-	*m*-TBHA	*m*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	68 (67)[9]
N-*p*-Tolylbenzo-	*p*-TBHA	*p*-$CH_3{\cdot}C_6H_4$—	C_6H_5—	112 (111)[8]
N-Phenyl-n-butyro-	P(n)BHA	C_6H_5—	CH_3-$(CH_2)_2$—	81 (81)[1]

* Reported values in brackets.

Table II.—Thermodynamic metal–ligand stability constants at 25°C

Complexing ion	Constant determined	Ligands				
		PBHA	*o*-TBHA	*m*-TBHA	*p*-TBHA	P(n)BHA
H^+	pK_a	11·04	11·12	11·12	11·13	11·45
Cu^{2+}	$\log K_1$	10·36	10·51	10·52	10·66	10·64
	$\log K_2$	8·78	8·85	8·86	8·79	8·87
	$\log (K_1/K_2)$	1·58	1·66	1·66	1·87	1·77
Zn^{2+}	$\log K_1$	7·51*	8·19	Ins.	Ins.	7·72
	$\log K_2$	6·63*	6·71			6·39
	$\log (K_1/K_2)$	0·88	1·48			1·33
Ni^{2+}	$\log K_1$	7·00*	7·64	Ins.	Ins.	7·61
	$\log K_2$	5·91*	6·06			5·69
	$\log (K_1/K_2)$	1·09	1·58			1·92
Mn^{2+}	$\log K_1$	6·02*	6·39	Ins.	Ins.	6·23
	$\log K_2$	5·15*	5·62			4·53
	$\log (K_1/K_2)$	0·87	0·77			1·70

Ins. = Insoluble.
* Calculated by Bjerrum-Calvin graphical method.
[Metal] 0·001*M*; [Ligand] 0·01*M*; [KOH] 0·1*M*.
Medium 50% (v/v) dioxan–water.

mixing the reagents or after addition of alkali. Attempts to determine their constants by decreasing the concentration of the metal ions to $5 \times 10^{-4}M$ did not succeed. In the acid range, Mn, Ni, and Zn complexes of PBHA gave maximum $\bar{n}$ values of 0·9. For such low values of $\bar{n}$, Goldberg's method[3] of calculation could not be applied and so the Bjerrum and Calvin graphical method was used. From the $\bar{n}$ values it appeared that precipitation started before formation of the 1:2 complex was complete. The stability constants were reproducible to 0·05 log units in replicate determinations, and variation of starting concentration of metal and ligand gave results varying by ±0·10 log units or less.

DISCUSSION

There was no evidence of metal ion hydrolysis, polynuclear complexes, protonated complexes, or influence of nitrate, chloride, perchlorate and alkali metal cations.

The Irving-Williams order of stabilities[4] was found to hold for all the systems with $K_1 > K_2$. The values of $\log K_1/K_2$ are consistently high for all copper complexes with a single exception. The $\Delta \log K$ value of 1·6–1·7 suggests that in these systems the electrostatic effect[5] has to be considered as well as the statistical effect (which gives $\log K = 0{\cdot}6$).

Values of $\log K$ for copper are considerably higher than for the other metals and the values for Zn are greater than those for Ni. The higher value for the copper chelate may be due to a square planar structure. The order Zn > Ni has been observed earlier[6] and attributed to steric hindrance preventing the formation of a square planar Ni complex. Also the hydrolysis constant of Zn is greater than that of Ni, indicating greater affinity of Zn^{2+} for hydroxide ions; the NOH group of the hydroxamic acid resembles the OH group. These factors seem to account for the order Zn > Ni.

Since all the metal ions are bivalent and of much the same size, the electrostatic contribution to the metal–ligand bond in the first complexes formed with the same ligand is assumed to be very nearly the same. The $\log K_1$ values for the P(n)BHA, PBHA and *o*-TBHA complexes were a linear function of the overall ionization potentials of Mn(II), Zn(II) and Ni(II) but the points for the Cu(II) complexes were always above the line, confirming the higher stability of the copper complexes. The values of $\log K_1/K_2$ imply that there is little or no steric hindrance to the addition of the second chelate group. A plot of the stability constants for Cu(II) *vs.* the ligand protonation constants is linear, the equation being $\log K = 0{\cdot}73\ pK_a + \text{constant}$. According to Jones and co-workers,[7] ligands with orbitals which can interact with suitable orbitals of the metal ion, give slopes greater than unity in such plots if the central ion has π-acceptor properties. They have further stated that Cu(II) and Ni(II) act as π-donors. The Cu(II) ion therefore seems to be acting as a π-donor.

The complexes of P(n)BHA with Zn, Ni and Mn(II) are less stable than the corresponding *o*-TBHA complexes, though P(n)BHA is more basic than *o*-TBHA. In contrast, the Cu(II) complexes follow the order of pK_a. Different geometries of the Cu and Zn, Ni and Mn complexes may be responsible for this unexpected behaviour in the stability order.

Acknowledgement—The authors are indebted to the authorities of Government Science Colleges, Jabalpur and Raipur for facilities. Grateful acknowledgement is made to the Chemical Society, London and van't Hoff fund, Amsterdam, for partial financial support. One of the authors (J. P. S.) is indebted to C.S.I.R., New Delhi for the award of a Junior Research Fellowhsip.

Department of Chemistry
Government College of Science
Raipur, M.P.
India

J. P. SHUKLA*
S. G. TANDON

Summary—Thermodynamic stability constants of complexes of Mn(II), Ni(II), Zn(II) and Cu(II) with five closely related *N*-arylhydroxamic acids have been determined at 25 ± 0·1° in 50% v/v aqueous dioxan medium. The stabilities of the complexes mostly follow the order of the basicity of the ligands and the electron affinities of the metal ions as measured by their second ionization potential.

Zusammenfassung—Die thermodynamischen Stabilitätskonstanten der Komplexe von Mn(II), Ni(II), Zn(II) und Cu(II) mit fünf nahe verwandte *N*-Arylhydroxamsäuren wurden bei 25 ± 0,1° in 50%(v/v) wäßrigem Dioxan gemessen. Die Stabilität der Komplexe schließt sich meistens an die Basizitätsreihenfolge der Liganden und an die Elektronenaffinitäten der Metallionen an, wie sie sich im zweiten Ionisierungspotential zeigen.

Résumé—On a déterminé les constantes de stabilité thermodynamique de complexes de Mn(II), Ni(II), Zn(II) et Cu(II) avec cinq acides *N*-arylhydroxamiques etroitement apparentés, à 25 ± 0,1° en milieu dioxane aqueux 50% v/v. Les stabilités des complexes suivent essentiellement l'ordre de basicité des ligands et les affinités électroniques des ions métalliques telles qu'elles sont mesurées par leur second potentiel d'ionisation.

REFERENCES

1. U. Priyadarshini and S. G. Tandon, *J. Chem. Eng. Data*, 1967, **12**, 143.
2. D. C. Bhura and S. G. Tandon, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2993.
3. D. E. Goldberg, *J. Chem. Educ.*, 1962, **39**, 328; 1963, **40**, 341.
4. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
5. N. Bjerrum, *Z. Physik. Chem.*, 1932, **106**, 238.
6. W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, 1954, **11**, 201, 301.
7. J. E. Jones, J. B. Poole, J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 1958, 2001, 2010.
8. S. G. Tandon and S. C. Bhattacharya, *J. Chem. Eng. Data*, 1962, **7**, 553.
9. V. K. Gupta, *Proc. Indian Science Congress, Roorkee, India*, 1965–66.

---

* Present address: Radiochemistry Division, Bhadha Atomic Research Centre, Trombay, Bombay-85 (AS).

Talanta, 1972, Vol. 19, p. 715. Pergamon Press. Printed in Northern Ireland

LETTERS TO THE EDITOR

Salicylaldehyde and β-resorcylaldehyde as indicators for DCTA titration of iron(III)

SIR,

Resorcylic acids have been used as indicators for the direct EDTA titration of ferric ions.[1] Salicylaldehyde and β-resorcylaldehyde have now been found suitable as indicators for the direct titration of iron(III) with DCTA. There is a sharp colour change from purple to deep yellow at the end-point. The optimum pH is 1·0–2·0, and 2 drops of 1% indicator solution give satisfactory results even in titration of 1 ml of 0·001*M* ferric nitrate with 0·001*M* DCTA. At pH 1·0, for 1·4 mg of iron, the following amounts of other ions could be tolerated: 140 mg of Na^+, K^+, NH_4^+, Cl^-, Br^-, ClO_4^-, NO_3^-, and SO_4^{2-}; 14 mg of Ag^+, Pb^{2+}, Al^{3+}, Ni^{2+} and Co^{2+}; 28 mg of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+} and Pd^{2+}; 7 mg of UO_2^{2+}, Zn^{2+} and Cd^{2+}; 1·4 mg of Cu^{2+}. Mn^{2+}, Zr^{4+}, Th^{4+} and anions forming stable complexes with iron(III), such as phosphates, vanadates, molybdates and tungstates, interfered at all levels. The process has been satisfactorily applied to the determination of ferric ions in ternary mixtures, iron ore and a drug. The suggested indicators are superior to Chrome Azurol S[2] with which aluminium interferes and thiocyanate[2] which can be used only under restricted conditions. With sulphosalicylic acid and tiron,[3] results are high by up to 4%.

M. N. DESAI
B. M. DESAI
B. S. PATWARI
M. H. GANDHI

Chemistry Department
Gujarat University
Ahmedabad-9
India

16 *September* 1971

REFERENCES

1. M. N. Desai, B. M. Desai and M. H. Gandhi, *Mikrochim. Acta*, 1970, 190.
2. L. W. Marple, *Talanta*, 1964, **11**, 1268.
3. F. Bermejo-Martínez and R. Mendora, *Quim. Ind. Bilboa*, 1959, **6**, 3; *Anal. Abstr.*, 1960, **6**, 4772

Talanta, 1972, Vol. 19, pp. 715 to 716. Pergamon Press. Printed in Northern Ireland

Potentiometric titration of sodium pentacyanonitrosylferrate(III)

SIR,

Sodium pentacyanonitrosylferrate(III) (sodium nitroprusside) is often used to detect acetaldehyde, hydrogen, sulphur and aliphatic amines in organic analysis as well as in end-point indication of mercurimetric titrations.[1] It is usually analysed argentometrically by the Mohr method.[2] We have investigated the possibility of potentiometric titration of sodium pentacyanonitrosylferrate(III) with mercury(II) or silver.

A Radelkis precision pH-meter type OP-205 (input resistance >1GΩ) was used. Indicator electrodes were silicone-rubber based halide-selective electrodes (OP-Cl-711, OP-Br-711, OP-I-711, OP-S-711), platinum needles (15 mm² surface area) and silver. The reference was a 0·1*M* calomel electrode. An agar-agar potassium nitrate salt bridge was used.

Mercuric nitrate solution, 0·05*M*, was made by warming 10·03 g of mercury of analytical purity with 50 ml of nitric acid (1 + 1) in a 500-ml flask on a water-bath until the appearance of nitrous fumes, setting the flask aside until the mercury had completely dissolved, then warming it on the water-bath until the nitrous fumes were completely expelled, and finally cooling and diluting to 1 litre.

In the procedure about 1·5 g of the material to be investigated is dissolved in water and diluted accurately to 100 ml. A 10-ml aliquot is diluted with 90 ml of water in a 150-ml beaker and titrated (magnetic stirring) with 0·05*M* mercuric nitrate or 0·1*M* silver nitrate.

Talanta, 1972, Vol. 19, p. 715. Pergamon Press. Printed in Northern Ireland

LETTERS TO THE EDITOR

Salicylaldehyde and β-resorcylaldehyde as indicators for DCTA titration of iron(III)

SIR,

Resorcylic acids have been used as indicators for the direct EDTA titration of ferric ions.[1] Salicylaldehyde and β-resorcylaldehyde have now been found suitable as indicators for the direct titration of iron(III) with DCTA. There is a sharp colour change from purple to deep yellow at the end-point. The optimum pH is 1·0–2·0, and 2 drops of 1% indicator solution give satisfactory results even in titration of 1 ml of 0·001*M* ferric nitrate with 0·001*M* DCTA. At pH 1·0, for 1·4 mg of iron, the following amounts of other ions could be tolerated: 140 mg of Na^+, K^+, NH_4^+, Cl^-, Br^-, ClO_4^-, NO_3^-, and SO_4^{2-}; 14 mg of Ag^+, Pb^{2+}, Al^{3+}, Ni^{2+} and Co^{2+}; 28 mg of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+} and Pd^{2+}; 7 mg of UO_2^{2+}, Zn^{2+} and Cd^{2+}; 1·4 mg of Cu^{2+}. Mn^{2+}, Zr^{4+}, Th^{4+} and anions forming stable complexes with iron(III), such as phosphates, vanadates, molybdates and tungstates, interfered at all levels. The process has been satisfactorily applied to the determination of ferric ions in ternary mixtures, iron ore and a drug. The suggested indicators are superior to Chrome Azurol S[2] with which aluminium interferes and thiocyanate[2] which can be used only under restricted conditions. With sulphosalicylic acid and tiron,[3] results are high by up to 4%.

M. N. DESAI
B. M. DESAI
B. S. PATWARI
M. H. GANDHI

Chemistry Department
Gujarat University
Ahmedabad-9
India

16 *September* 1971

REFERENCES

1. M. N. Desai, B. M. Desai and M. H. Gandhi, *Mikrochim. Acta*, 1970, 190.
2. L. W. Marple, *Talanta*, 1964, **11**, 1268.
3. F. Bermejo-Martínez and R. Mendora, *Quim. Ind. Bilboa*, 1959, **6**, 3; *Anal. Abstr.*, 1960, **6**, 4772

Talanta, 1972, Vol. 19, pp. 715 to 716. Pergamon Press. Printed in Northern Ireland

Potentiometric titration of sodium pentacyanonitrosylferrate(III)

SIR,

Sodium pentacyanonitrosylferrate(III) (sodium nitroprusside) is often used to detect acetaldehyde, hydrogen, sulphur and aliphatic amines in organic analysis as well as in end-point indication of mercurimetric titrations.[1] It is usually analysed argentometrically by the Mohr method.[2] We have investigated the possibility of potentiometric titration of sodium pentacyanonitrosylferrate(III) with mercury(II) or silver.

A Radelkis precision pH-meter type OP-205 (input resistance $>1 G\Omega$) was used. Indicator electrodes were silicone-rubber based halide-selective electrodes (OP-Cl-711, OP-Br-711, OP-I-711, OP-S-711), platinum needles (15 mm^2 surface area) and silver. The reference was a 0·1*M* calomel electrode. An agar-agar potassium nitrate salt bridge was used.

Mercuric nitrate solution, 0·05*M*, was made by warming 10·03 g of mercury of analytical purity with 50 ml of nitric acid (1 + 1) in a 500-ml flask on a water-bath until the appearance of nitrous fumes, setting the flask aside until the mercury had completely dissolved, then warming it on the water-bath until the nitrous fumes were completely expelled, and finally cooling and diluting to 1 litre.

In the procedure about 1·5 g of the material to be investigated is dissolved in water and diluted accurately to 100 ml. A 10-ml aliquot is diluted with 90 ml of water in a 150-ml beaker and titrated (magnetic stirring) with 0·05*M* mercuric nitrate or 0·1*M* silver nitrate.

Talanta, 1972, Vol. 19, p. 715. Pergamon Press. Printed in Northern Ireland

LETTERS TO THE EDITOR

Salicylaldehyde and β-resorcylaldehyde as indicators for DCTA titration of iron(III)

SIR,

Resorcylic acids have been used as indicators for the direct EDTA titration of ferric ions.[1] Salicylaldehyde and β-resorcylaldehyde have now been found suitable as indicators for the direct titration of iron(III) with DCTA. There is a sharp colour change from purple to deep yellow at the end-point. The optimum pH is 1·0–2·0, and 2 drops of 1% indicator solution give satisfactory results even in titration of 1 ml of 0·001*M* ferric nitrate with 0·001*M* DCTA. At pH 1·0, for 1·4 mg of iron, the following amounts of other ions could be tolerated: 140 mg of Na^+, K^+, NH_4^+, Cl^-, Br^-, ClO_4^-, NO_3^-, and SO_4^{2-}; 14 mg of Ag^+, Pb^{2+}, Al^{3+}, Ni^{2+} and Co^{2+}; 28 mg of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+} and Pd^{2+}; 7 mg of UO_2^{2+}, Zn^{2+} and Cd^{2+}; 1·4 mg of Cu^{2+}. Mn^{2+}, Zr^{4+}, Th^{4+} and anions forming stable complexes with iron(III), such as phosphates, vanadates, molybdates and tungstates, interfered at all levels. The process has been satisfactorily applied to the determination of ferric ions in ternary mixtures, iron ore and a drug. The suggested indicators are superior to Chrome Azurol S[2] with which aluminium interferes and thiocyanate[2] which can be used only under restricted conditions. With sulphosalicylic acid and tiron,[3] results are high by up to 4%.

M. N. DESAI
B. M. DESAI
B. S. PATWARI
M. H. GANDHI

Chemistry Department
Gujarat University
Ahmedabad-9
India

16 *September* 1971

REFERENCES

1. M. N. Desai, B. M. Desai and M. H. Gandhi, *Mikrochim. Acta*, 1970, 190.
2. L. W. Marple, *Talanta*, 1964, **11**, 1268.
3. F. Bermejo-Martínez and R. Mendora, *Quim. Ind. Bilboa*, 1959, **6**, 3; *Anal. Abstr.*, 1960, **6**, 4772

Talanta, 1972, Vol. 19, pp. 715 to 716. Pergamon Press. Printed in Northern Ireland

Potentiometric titration of sodium pentacyanonitrosylferrate(III)

SIR,

Sodium pentacyanonitrosylferrate(III) (sodium nitroprusside) is often used to detect acetaldehyde, hydrogen, sulphur and aliphatic amines in organic analysis as well as in end-point indication of mercurimetric titrations.[1] It is usually analysed argentometrically by the Mohr method.[2] We have investigated the possibility of potentiometric titration of sodium pentacyanonitrosylferrate(III) with mercury(II) or silver.

A Radelkis precision pH-meter type OP-205 (input resistance $>1 G\Omega$) was used. Indicator electrodes were silicone-rubber based halide-selective electrodes (OP-Cl-711, OP-Br-711, OP-I-711, OP-S-711), platinum needles (15 mm^2 surface area) and silver. The reference was a 0·1*M* calomel electrode. An agar-agar potassium nitrate salt bridge was used.

Mercuric nitrate solution, 0·05*M*, was made by warming 10·03 g of mercury of analytical purity with 50 ml of nitric acid (1 + 1) in a 500-ml flask on a water-bath until the appearance of nitrous fumes, setting the flask aside until the mercury had completely dissolved, then warming it on the water-bath until the nitrous fumes were completely expelled, and finally cooling and diluting to 1 litre.

In the procedure about 1·5 g of the material to be investigated is dissolved in water and diluted accurately to 100 ml. A 10-ml aliquot is diluted with 90 ml of water in a 150-ml beaker and titrated (magnetic stirring) with 0·05*M* mercuric nitrate or 0·1*M* silver nitrate.

TABLE I.—REPRODUCIBILITY OF THE POTENTIOMETRIC DETERMINATION OF SODIUM NITROPRUSSIDE

	Electrode	Cathodically polarized Pt	Ag	Cathodically polarized Ag	OP-Cl-711	OP-Br-711	OP-I-711	OP-S-711
Average error, %	Hg(II) titrant	0·17	0·27	—	0·28	0·24	0·23	0·25
	Ag titrant	—	0·23	0·19	0·24	0·22	0·22	0·20

From the potentiometric titration curves obtained in our experiments it can be stated that cathodically polarized platinum electrodes, silver electrodes and silicone-rubber based halide-selective membrane electrodes[3] can all be used as indicator electrodes for the mercurimetric titration, but the platinum electrode gives the best potential jump and the best precision (Table I). The cathodically polarized silver electrode is best for the argentometric titration. However, the differences in precision are so small that any of the electrodes tried would be suitable.

County Institute for Food Control
and Chemical Analysis
Székesfehérvár, Hungary
E. SISKA

Institute for General and
Analytical Chemistry
Technical University
Budapest, Hungary
E. PUNGOR

27 *August* 1971

REFERENCES

1. E. Votoček, *Chem. Ztg.* 1918, **42**, 257, 271, 317.
2. *Prüfung der chemischen Reagenzien auf Reinheit*, 5th Ed., Merck, Darmstandt, 1939.
3. E. Pungor and K. Tóth, *Analyst*, 1970, **95**, 625.

Talanta, 1972, Vol. 19, p. 715. Pergamon Press. Printed in Northern Ireland

LETTERS TO THE EDITOR

Salicylaldehyde and β-resorcylaldehyde as indicators for DCTA titration of iron(III)

SIR,

Resorcylic acids have been used as indicators for the direct EDTA titration of ferric ions.[1] Salicylaldehyde and β-resorcylaldehyde have now been found suitable as indicators for the direct titration of iron(III) with DCTA. There is a sharp colour change from purple to deep yellow at the end-point. The optimum pH is 1·0–2·0, and 2 drops of 1% indicator solution give satisfactory results even in titration of 1 ml of 0·001*M* ferric nitrate with 0·001*M* DCTA. At pH 1·0, for 1·4 mg of iron, the following amounts of other ions could be tolerated: 140 mg of Na^+, K^+, NH_4^+, Cl^-, Br^-, ClO_4^-, NO_3^-, and SO_4^{2-}; 14 mg of Ag^+, Pb^{2+}, Al^{3+}, Ni^{2+} and Co^{2+}; 28 mg of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Be^{2+} and Pd^{2+}; 7 mg of UO_2^{2+}, Zn^{2+} and Cd^{2+}; 1·4 mg of Cu^{2+}. Mn^{2+}, Zr^{4+}, Th^{4+} and anions forming stable complexes with iron(III), such as phosphates, vanadates, molybdates and tungstates, interfered at all levels. The process has been satisfactorily applied to the determination of ferric ions in ternary mixtures, iron ore and a drug. The suggested indicators are superior to Chrome Azurol S[2] with which aluminium interferes and thiocyanate[2] which can be used only under restricted conditions. With sulphosalicylic acid and tiron,[3] results are high by up to 4%.

M. N. DESAI
B. M. DESAI
B. S. PATWARI
M. H. GANDHI

Chemistry Department
Gujarat University
Ahmedabad-9
India

16 *September* 1971

REFERENCES

1. M. N. Desai, B. M. Desai and M. H. Gandhi, *Mikrochim. Acta*, 1970, 190.
2. L. W. Marple, *Talanta*, 1964, **11**, 1268.
3. F. Bermejo-Martínez and R. Mendora, *Quim. Ind. Bilboa*, 1959, **6**, 3; *Anal. Abstr.*, 1960, **6**, 4772

Talanta, 1972, Vol. 19, pp. 715 to 716. Pergamon Press. Printed in Northern Ireland

Potentiometric titration of sodium pentacyanonitrosylferrate(III)

SIR,

Sodium pentacyanonitrosylferrate(III) (sodium nitroprusside) is often used to detect acetaldehyde, hydrogen, sulphur and aliphatic amines in organic analysis as well as in end-point indication of mercurimetric titrations.[1] It is usually analysed argentometrically by the Mohr method.[2] We have investigated the possibility of potentiometric titration of sodium pentacyanonitrosylferrate(III) with mercury(II) or silver.

A Radelkis precision pH-meter type OP-205 (input resistance >1GΩ) was used. Indicator electrodes were silicone-rubber based halide-selective electrodes (OP-Cl-711, OP-Br-711, OP-I-711, OP-S-711), platinum needles (15 mm² surface area) and silver. The reference was a 0·1*M* calomel electrode. An agar-agar potassium nitrate salt bridge was used.

Mercuric nitrate solution, 0·05*M*, was made by warming 10·03 g of mercury of analytical purity with 50 ml of nitric acid (1 + 1) in a 500-ml flask on a water-bath until the appearance of nitrous fumes, setting the flask aside until the mercury had completely dissolved, then warming it on the water-bath until the nitrous fumes were completely expelled, and finally cooling and diluting to 1 litre.

In the procedure about 1·5 g of the material to be investigated is dissolved in water and diluted accurately to 100 ml. A 10-ml aliquot is diluted with 90 ml of water in a 150-ml beaker and titrated (magnetic stirring) with 0·05*M* mercuric nitrate or 0·1*M* silver nitrate.

TABLE I.—REPRODUCIBILITY OF THE POTENTIOMETRIC DETERMINATION OF SODIUM NITROPRUSSIDE

	Electrode	Cathodically polarized Pt	Ag	Cathodically polarized Ag	OP-Cl-711	OP-Br-711	OP-I-711	OP-S-711
Average error, %	Hg(II) titrant	0·17	0·27	—	0·28	0·24	0·23	0·25
	Ag titrant	—	0·23	0·19	0·24	0·22	0·22	0·20

From the potentiometric titration curves obtained in our experiments it can be stated that cathodically polarized platinum electrodes, silver electrodes and silicone-rubber based halide-selective membrane electrodes[3] can all be used as indicator electrodes for the mercurimetric titration, but the platinum electrode gives the best potential jump and the best precision (Table I). The cathodically polarized silver electrode is best for the argentometric titration. However, the differences in precision are so small that any of the electrodes tried would be suitable.

County Institute for Food Control
and Chemical Analysis
Székesfehérvár, Hungary
E. SISKA

Institute for General and
Analytical Chemistry
Technical University
Budapest, Hungary
E. PUNGOR

27 *August* 1971

REFERENCES

1. E. Votoček, *Chem. Ztg*. 1918, 42, 257, 271, 317.
2. *Prüfung der chemischen Reagenzien auf Reinheit*, 5th Ed., Merck, Darmstandt, 1939.
3. E. Pungor and K. Tóth, *Analyst*, 1970, 95, 625.

Talanta, 1972, Vol. 19, pp. 717 to 746. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

REACTION RATE METHODS IN ANALYSIS

HARRY B. MARK, JR.
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(*Received* 22 *June* 1971. *Accepted* 30 *October* 1971)

Summary—A review is given of the principles and application of catalytic and reaction rate methods of analysis.

AS INSTRUMENTATION technology, measurement techniques, electronic circuitry, and analytical procedures have advanced in recent years to a very high degree of development, the accuracy and precision necessary to make dynamic reaction systems applicable to both routine and special analytical problems have become available. Thus, there has been considerable research by a fairly large number of analytical chemists on the development of instrumentation, methods, and applications of kinetic (dynamic) based analyses for both new and old analytical problems. In fact, some analytical chemists, the author included, have been heard to say that these advances in instrumentation and electronic circuitry have "opened up a completely *new* area of research in analytical chemistry." Such a statement is not really accurate, of course, as kinetic based methods of analysis have been used for many years by clinical chemists for enzyme assay and other biological and medical tests. It would be more correct to say that analytical chemists have recently realized the tremendous potential in the application of kinetic methods and are now opening up new areas and applications for these methods. Also they are actively engaged in improving the sensitivity as well as the accuracy and precision of such methods. This realization of the potential of kinetics in analysis came about when it was recognized that kinetic based procedures have several inherent properties which can be used advantageously in analysis.

First, analytical chemists have long realized that in a real analytical problem, the species to be determined is rarely found unaccompanied by one or more substances that are closely related chemically and/or physically, and generally separation techniques must be used, which are often laborious and lead to considerable error in the analysis. There are also cases, such as the analysis of the ratio of different functional groups in the same polymer molecules, where non-destructive separation is impossible. Thus, it is clear that the analysis should (or must) be performed without prior separation.

Methods for *in situ* analysis of a mixture of species having similar properties can be classified as either thermodynamic (equilibrium) or kinetic (dynamic) depending on the method used to eliminate or reduce the interference of the other components of the mixture. A thermodynamic masking involves the alteration of the equilibrium conditions of the solution in such a way as to render all reactions, except the one(s) of analytical interest, thermodynamically unfavoured. The kinetic approach involves

---

* For reprints of this Review, see Publisher's announcement near the end of the issue.

utilizing differences in the reaction rates (or adjusting them if necessary) to isolate the reactions(s) of analytical interest. The thermodynamic differences in reactions of closely related compounds, such as homologues or isomers, with a common reagent are often much too small to be used for analysis of mixtures. However, the kinetic differences are usually quite large and permit either individual or simultaneous *in situ* analysis of the components of the mixture. This arises from the fact that the free energy of activation and hence the rate constant for any reaction is very dependent on the effect of structure of the reactants on formation of the activated complex, *etc.* Thus, reactions of closely related species which differ slightly in structure will often have essentially the same net change in free energy for the overall reaction but will reach equilibrium at widely varying rates. Also, changes in temperature, solvent characteristics, activity changes, *etc.*, have much larger effects on the relative rate constants of similar species than they do on the relative values of the equilibrium constants.

Secondly, a large number of inorganic and organic reactions can now be used in analysis. Many chemical reactions are not sufficiently uniform in behaviour to be used in equilibrium-based methods as they attain equilibrium slowly, have side-reactions, or are not sufficiently quantitative (the formation constants are too small) to be applicable. However, the same reactions can be used easily under initial reaction-rate conditions (explained below in the text). Also catalytic kinetic methods are considerably more sensitive than equilibrium methods, and kinetic-based enzymatic reactions are often extremely selective for a particular substrate.

On the other hand, kinetic techniques have one obvious and serious disadvantage. Any dynamic measurement includes time as an experimental variable, which is not the case in equilibrium measurement. It is probably this consideration that has made analytical chemists in the past somewhat afraid of using kinetics as an analytical tool. However, recent developments in instrumentation, especially in computer-based data analysis, signal-averaging and automation have overcome this fear of lower measurement accuracy.

As a result of this increase in interest, several books have been recently published on various aspects of the subject.[1–5] Mark, Rechnitz and Greinke[1] published a comprehensive text on kinetic analytical techniques and mechanistic studies related to analysis problems, Yatsimirskii[2] has given an extensive compilation and discussion of the application of catalytic reactions in trace analysis, and Guilbault,[3] Bergmeyer,[4] and Ruyssen and Vandenriesche[5] have written texts covering the area of enzymatic reactions in analysis. There have also been monograph chapters by Blaedel and Hicks,[6] Mark, Papa and Reilley,[7] Janata,[8] Pardue[9] and Crouch[10] on various aspects of kinetic analysis. The last two are especially significant as they deal with the principles and advances in instrumentation designed *specifically* for kinetic analysis, There have also been the extensive review articles by Rechnitz,[11–13] Guilbault,[14–17] Bergmeyer,[18] Devlin[19] and Roth[20] on various aspects of kinetic analysis in chemistry and clinical chemistry.

Because the early literature on reaction rate techniques applied to chemical analysis is very well reviewed in the publications cited, this review will generally cover only the literature contributions of the past 2–5 years, though particularly important earlier work will be cited.

The topics reviewed individually are recent advances in methods of kinetic analysis, new procedures and approaches to chemical analysis, and reports of kinetic studies of systems which are of specific interest and/or application to analysis. (The huge literature concerned with fundamental kinetic studies of reaction kinetics and mechanisms will not be reviewed.)

MATHEMATICAL BASIS OF KINETIC METHODS OF ANALYSES

A very large number of methods for the calculation of the initial concentration(s) of the species of interest from reaction rate data have been developed over the past few years. These methods involve, in general, simple mathematical manipulation and rearrangement of the usual differential or integral forms of the classical reaction rate equations. With few exceptions most have been reported within the past 5—10 years. They can be classified in two main categories: methods for a single species and methods for the simultaneous *in situ* analysis of mixtures. Within each category, the methods can be subdivided according to the kinetic order of the reactions: pseudo zero-order or initial rate methods, first-order and pseudo first-order methods, and second-order techniques. The principles, mathematical treatments, applicability and limitations of these methods have been discussed in some of the works already cited.[1,6,7,9,10] Recent papers are reviewed below.

Methods for determination of a single species

Pseudo zero-order methods. This approach is the most commonly used in routine and special applications, partly owing to the simplicity of the calculations and the fact that essentially all catalytic methods, both chemical and enzymatic, use pseudo zero-order conditions during the rate measurement. The principle of the initial-rate methods is simple as they are based on taking measurements only during the initial 1–3% or so of total reaction. Under these conditions the amount of reactant consumed and product formed is negligible (*i.e.*, the concentration of the reactants does not change appreciably during the period of the rate measurement) and hence the rate curve is essentially linear, its slope being proportional to the concentration of the reactant being determined.[1,6,7,9,10] There are other advantages besides simplicity of calculation. First , the reverse reaction can be ignored, and secondly, complications such as side-reactions are minimal. Three initial-rate methods are described in the literature. The direct approach is the derivative slope method where the rate of the reaction is measured by electronic derivative circuitry.[9,10,21,22] Margerum and co-workers[23–25] have described a stopped-flow derivative method for determination of a single species. This technique uses repetitive slope measurement during each run, and signal-averaging by a built-in computer to improve the analytical results. In the second approach, essentially a two-point method called the fixed-time method,[1,6,7,9,10] the change in concentration of product (output signal) is measured over a fixed time-interval, giving $(\Delta C/\Delta t)$ which is, of course, the slope of the rate curve. The third approach is also a two-point method, the variable-time method.[1,6,7,9,10] In this method the time interval, Δt, required for the output signal to vary between two fixed values (ΔC) is measured. These three initial reaction rate methods have been used for both catalysed and uncatalysed reactions.[1,6,9] The concentrations of the catalyst (including enzymes) as well as of catalyst activators and inhibitors have been determined.[1,3,9,17]

First-order and pseudo first-order methods. Crouch has discussed the principles and parameters of importance for a non-linear response variable-time procedure for first-order and pseudo first-order reactions.[10] Mark, Rechnitz and Greinke[1] have also discussed the criteria for neglecting the contributions of either faster or slower-reacting components in the kinetic determination of a single species in a mixture. Janata and Mark[25a] have suggested analogue simulation techniques for the analysis of such rate curves.

Second-order methods. Very little work has been reported on the analytical applications of second-order conditions for determination of a single species. Weichselbaum *et al.*[21] have described derivative methods in which the maximum rate observed during an autocatalysed reaction run under second-order conditions was applicable for the determination of ammonia and blood-urea nitrogen. Janata and Mark[25a] have also discussed analogue simulation of second-order rate curves for determination of initial concentrations.

Methods for the simultaneous in situ *analysis of mixtures*

The development of methods for the *in situ* simultaneous determination of closely related components of mixtures has received considerable attention. As discussed in the instrumentation section, the tremendous advances in the accuracy and precision of rate measurements makes these methods practical.

Pseudo zero-order methods. Mark has reported an initial reaction rate method for the simultaneous assay of two alcohols, using enzyme-catalysed reactions.[26] Guilbault and co-workers[17,27,28] have reported a very effective method for the *in situ* analysis of multicomponent mixtures of a large variety of different and closely related substrates by taking advantage of enzyme catalysis selectivity.

First-order and pseudo first-order methods. Though each of the methods developed for reactions of this type is applicable to true first-order reactions, all the applications reported, with the exception of radionuclide decay reactions, are to second-order reactions run under pseudo first-order conditions (where either the reactants or the reagents are in very large excess and, hence, do not change appreciably in concentration during the course of the reaction).[1] A graphical method (called the logarithmic extrapolation method) based on the extrapolation of a typical first-order log response *vs.* time plot of the total rate curve has been described for binary mixtures where the reagent is in large excess with respect to the total concentration of the unknown in the mixture.[1] Lee and Kolthoff have described a mathematical single-point method based on a single measurement made at a fixed time during the reaction, for the same pseudo first-order conditions.[29] Garmon and Reilley have described a very simple and successful method of proportional equations based on the principle of constant fractional life.[1,7,30] This method is applicable to both simple and complex first-order reaction sequences. Margerum and co-workers[23-25,31] have described a continuous measurement approach to the method of proportional equations which is more accurate than the finite point approach of Garmon and Reilley[1,30] and have extended the method successfully to three-component mixtures. Roberts and Regan[32] have devised a mathematical single-point rate measurement procedure and Greinke and Mark[33] have devised a method of proportional equations for the reaction condition which is pseudo first-order with respect to the reagent concentration ($[\text{reagent}] \ll [\text{mixture}]$).

Second-order methods. Siggia and Hanna[34] have devised a second-order graphical (logarithmic) extrapolation procedure for the complete analysis of binary mixtures, the reagent and reactant concentrations being of the same order of magnitude. Reilley and Papa developed a second-order linear extrapolation method for the special case where [mixture] = [reagent].[35] For both of these second-order systems Reilley and Papa[35] and Papa, Mark and Reilley[36] have developed mathematical single-point and double-point methods which eliminate the need for a graphical plot. Lee and Kolthoff[29] have developed a different mathematical single-point method for the special case [mixture] = [reagent]. Schmalz and Geiseler[37–40] have reported a graphical differential method and graphical integral method for second-order reactions. They have presented several different modifications of each method.

Applicability and limitations of the various methods for the analysis of mixtures. As can be seen above, many different methods have been reported in recent years. These methods not only employ different reaction order conditions, but also use different mathematical and/or graphical methods of data manipulation and display and some make certain experimental and mathematical assumptions. The choice of the best method and conditions for a specific problem is not intuitively obvious,[1] and considerable work on this problem has recently been reported. Ingle and Crouch have examined the relative merits and limitations of the fixed-time and variable-time methods of data treatment for catalytic and pseudo first-order reaction procedures.[41] They have shown that the fixed-time method is preferable for first- or pseudo first-order reactions and substrate determinations in catalytic reactions. However, their error analysis shows that the variable-time approach is best for enzyme and catalyst determinations and also for non-linear response-rate curves. Reilley and Papa[35] and Papa, Mark and Reilley[36] have discussed the optimum conditions for the second-order linear and graphical extrapolation methods. Mark, Greinke and co-workers[1,36,42,43] have developed a very detailed error analysis for all the first-order and pseudo first-order methods discussed above. They have shown that for binary mixtures the choice of the best method for a particular mixture and of the optimum analysis conditions and experimental parameters of the chosen method was strongly dependent on the ratio of the rate constants as well as on the ratio of the initial concentrations of the species of interest in the mixture. They also gave a set of rules of thumb[1,42] for use as rapid guide lines for the choice of method and optimum conditions. There have also been a few experimental comparisons of the results obtained by using some of the pseudo first-order methods,[1,44–46] which are in general agreement with the theoretical predictions of the error analysis treatments. Siggia and Hanna[47] and Greinke and Mark[48] have also discussed the relative influence of synergistic effects on the accuracy of the various first-order and pseudo first-order methods. Such effects can often be ignored in graphical extrapolation methods, but can lead to huge errors in any of the non-graphical methods. Greinke and Mark[48] point out that when a non-graphical method is used it is absolutely necessary to have a very complete understanding of all the chemistry of the reactions employed.

Recently there has been a very important series of papers by Margerum and co-workers on the parameters affecting the accuracy of the simultaneous analysis of mixtures by pseudo first-order reaction methods.[23–25,31] Their conclusions are that their approach to the problem is the superior method in several examples of the use of reaction rate methods for analysis. In the early development of differential reaction rate methods for the simultaneous *in situ* analysis of mixtures of closely related substances, the chemical reactions used were not suitable for continuous automatic measurement of the entire rate response curves,[1,7] and calculations were generally done by hand. Hence, the emphasis at that time in the development of the reaction rate methods was on minimizing the number of experimental points taken and on predetermining the optimum times, *etc.*, for taking the readings.[1,7] However, in recent years the advances in electronic circuitry and computer technology have had a tremendous influence on the design of instrumentation for kinetic analysis. These instrumental advances have also had a strong influence on the principles and approaches to differential rate methods. Margerum and co-workers[23–25,31] (and also Weichselbaum and co-workers[21,49]) have shown conclusively that the use of built-in computation systems allows continuous analysis of the entire reaction rate curve. The results are thus immediately processed with both ensemble averaging and smoothing routines. Experimental results and detailed error analysis have shown that this approach to data acquisition, reduction and display leads to a much greater accuracy and precision of the analytical results.[23–25,31] In fact, good results can be obtained for fast reaction differential rate analyses where the usual finite or minimal data point methods fail completely.[23,31] Obviously, this approach will be that used in most future developments in kinetic-based methods of analysis.

INSTRUMENTATION

As mentioned above, the major reason for the considerable increase in practical applications of kinetic-based methods is the tremendous advance that has been made in quantitative chemical instrumentation and electronics in the past few years, especially the efforts of instrument manufacturers and certain research groups to design instruments which apply these technological advances to meet the special features and demands of kinetic measurements on dynamic systems. Perhaps the most important of these advances is a consequence of the fantastic developments in both analogue and digital computer technology, as a result of which low-cost linear and digital integrated circuits have been made readily available to people interested in designing chemical instrumentation for ultrasensitive measurement. To quote a statement in a recent publication by Crouch,[10] the availability of integrated circuits "is revolutionizing instrumentation in science."

The instrumental advances can be classified in three separate but overlapping categories. First there are the improvements in the accuracy and precision of the reaction monitoring system electronics such as the excitation and transducer response circuits which create and measure the signal which is proportional to some time-dependent parameter in the chemical reaction (*e.g.*, improved stabilization of spectrophotometer light sources and increases in the sensitivity of photoelectric transducer circuitry). Secondly, the availability of low-cost computing elements has made it possible to build into the instruments either limited or elaborate self-contained computing capability. The extent and elaboration of the computation capability is, of course, reflected in the price of the instrument. These built-in computers can vary from a simple device to convert an initial-rate slope into a digital display of the concentration of the species to be determined, to a full-scale computing device which not only handles data reduction but also controls the operation and timing of the sequencial operations in the experiment. In the extreme case, the computing device operates in a feed-back mode and can sample and analyse results during the course of an experiment and then alter the experimental control parameters in such a way as to optimize the sensitivity and/or selectivity of the determination. The third area of advance is in automation design. This includes advances in the mechanical design and accuracy of sampling units, reagent addition and mixing procedures, *etc*, as well as the application of computing devices to start, control and time the automated procedures and devices (which illustrates the overlap of the three categories).

In the area of new developments in instrumentation of kinetic methods of analysis, there have been two excellent monograph chapters published recently which discuss the basic principles and applications of analogue–digital circuitry employed in considerable detail data reduction and automation design.[9,10] The chapter by Crouch[10] is especially comprehensive and clear in its discussion of computer-based kinetic method instrumentation.

Reaction monitoring

System electronic circuitry. The first problem in improving the accuracy and precision of kinetic-based analytical results is improving the quantitative nature of the total reaction monitoring system (spectrophotometric, potentiostatic, conductometric, *etc.*) and modifying it specifically for time-dependent measurements in following reaction rates. It is convenient to discuss the advances according to the type of measurement system.

Spectrophotometric systems. One of the major problems in adapting spectrophotometric instrumentation to kinetic measurement is that of light-source variation. This problem is inherent in any spectrophotometric system and even though this technique is relatively simple and generally applicable, it has caused kineticists in the past to shy away from spectrophotometric systems for accurate measurement, because such light-fluctuations are often of the same or similar time period as the reaction being followed.[21,49] Most commercial spectrophotometers which are designed for time-independent spectral measurements minimize such light-source variations by the use of double-beam optical systems which partially cancel fluctuations by periodic comparison of reference and sample beam intensities. Such double-beam systems have not generally been considered suitable for spectrophotometric instruments specifically designed for reaction rate measurement. Such systems seriously limit the response-time of the instrument, tend to introduce significant noise, and also add to the cost and complexity of the instrument,[10,21,49] so most designs for kinetics instrumentation employ a single-beam (non-wavelength-scanning) system and concentrate on lamp stabilization.

Weichselbaum and co-workers[21,49] have described a simple stabilization system which regulates the lamp voltage. This circuit compensates for variations in the lamp filament resistance and is thus more efficient than the more common techniques which regulate only the applied voltage or the applied current. Further stabilization is achieved by having a thermal convection baffle in the lamp housing. This source system was reported to give a drift of less than 0·003 absorbance units per hour.

As the stabilization method of Weichselbaum *et al.*[21,49] controls the lamp electrical input and does not directly control the actual lamp output intensity, an uncertainty is introduced into the measurement. Loach and Loyd,[50] and Pardue and co-workers[51,52] have reported several different circuits which use an optical feed-back system for lamp stabilization. The lamp output beam is split and one beam is monitored by means of a photomultiplier tube, the signal from which is fed back to the lamp power supply as an error signal which modifies the power supply voltage to maintain a constant intensity output. Fluctuation of less than 0·03% transmission per hour has been attained.[50]

The elimination of detector noise and drift is also a critical problem in the application of a spectrophotometric system to kinetic analysis, especially if the derivative of the rate curve is being determined by a built-in computation module or unit[21,49] as discussed in a later section. Weichselbaum and co-workers[21,49] discussed the relative signal-to-noise ratios for photodiode tubes and photomultiplier tubes in some detail. They found that when both types of phototransducer are operated at the same anode current, the photodiode tube has a higher signal-to-noise ratio than the photomultiplier. They concluded that the photodiode tube was thus more applicable in non-wavelength-scanning spectrometers designed for kinetic measurement, where light source intensity is not a limiting factor. Crouch and co-workers[10,53] have pointed out correctly that this evaluation of comparative applicability from signal-to-noise ratios at constant anode current is not valid for all spectrophotometric uses. They demonstrated that for systems where the light level is low and/or cannot be controlled, a photomultiplier gives better results. Weichselbaum and co-workers[21,49] have also reported that vacuum phototubes have more favourable signal-to-noise ratios than similar gas-filled tubes. A recent paper by Franklin, Horlick and Malmstadt[54] discusses the optimum criteria for stability of the power supply to the detector.

Recently, fluorimetric methods for kinetic analysis of a variety of materials, mainly of a biological nature, have also been developed.[10,55,56] This technique, although less general in application, has inherent advantages over normal absorbance spectrophotometry in that it is considerably more sensitive for certain high-efficiency fluorescent systems, and in dilute solution the fluorescence intensity is directly proportional to chemical concentration, which reduces signal processing (linearization) significantly. Though so far no papers have been published specifically describing special electronic circuit design and modification of standard fluorimeters for kinetic measurement, it can be stated that similar criteria and/or requirements for detector noise and drift and excitation light-source reproducibility are the same as discussed above for spectrophotometric measurements.

Electrometric systems. Because of the simplicity and ease of making highly accurate current or voltage measurements (made possible by analogue operational amplifier circuitry[57]) considerable work has recently been done on adaptation of potentiometric, constant-current coulometric, and amperometric monitoring of reaction rates for analytical determinations. Some of the early work on potentiometric measurement used a concentration cell technique.[58] Rechnitz and co-workers[59–64] have described the applications of various ion-selective electrodes in potentiometric measurement of reaction rates and kinetic analysis. They have also reported the application of a fast-response, high input-impedance, differential amplifier circuit for kinetic measurement, using two different ion-selective electrodes as the potentiometric cell.[59] Janata and Mark have suggested the application of constant-current coulometric techniques for simultaneous differential reaction rate analysis.[25a] Pardue has described the application of a polarized rotating platinum electrode system using amperometric detection for kinetic-based determinations.[65]

Conductometric instrumentation based on operational amplifier circuitry has also been described for use in kinetic methods of analysis.[66–69] Recently a bipolar-pulse modification of conductometric measurement has been described by Johnson and Enke.[70] This technique seems to be very promising for rate measurement because of its great sensitivity to small changes in conductance.

Reaction temperature control apparatus. As essentially all chemical reaction rates are very strongly dependent on temperature, considerable effort has been made to design simple but highly reliable thermostatic reaction cells and convenient but accurate temperature control systems (generally water-baths). A very comprehensive discussion of the design and construction of temperature control systems has been given by Van Swaay.[71,72]

Pardue and Rodriguez[51] designed a spectrophotometer cell which was sealed into a Lucite outer jacket which allowed water from a thermostatic bath to be in direct contact with the spectrophotometer cell walls. This permitted rapid temperature equilibration of the reactant solutions mixed by stirring in the cell. Weichselbaum and co-workers[21,49] described a spectrophotometer cell which had a separate mixing chamber above the cell itself. Both compartments were thermostatically controlled and the mixing chamber was fitted with an effective magnetic induction stirrer. Very rapid temperature equilibration on mixing of reagents was reported. Feil *et al.*[73] have reported a rapid temperature equilibration cell specifically designed for use with the Beckman DU spectrophotometer. Excellent temperature regulation ($\pm 0{\cdot}005°$ at 25°) was attained.

Weichselbaum, Smith and Mark[74] described a proportional dual thermistor bridge temperature-control system using analogue–digital control circuitry. With use of the jacketed cell described above,[21,49] better than $\pm 0{\cdot}01°$ regulation in the cell was attained at various temperatures. The system was designed so that four different controlled temperatures (15°, 25°, 30°, and 37°) could be attained automatically in a few minutes by simply pushing a selector switch.

Data reduction and display systems

In the application of kinetic methods to routine analysis the detector signal response being used to follow the course of the chemical reaction must be converted into some convenient form, ideally directly into the concentration of the species being determined. Consequently a large volume of research on this has been reported. Systems described vary from the very simple to virtually a built-in digital computer unit.

Computation systems for initial reaction rate methods. Most practical reaction rate based procedures (enzymatic and other clinical assay methods in particular) measure only the initial 1–3% of the overall reaction rate curve, primarily because the mechanism and hence the kinetics are well-behaved in the early stages and the initial rate is essentially constant (pseudo zero-order) with time over this period and is directly proportional to the concentration of the species to be determined. (Detailed discussions of the theory and principles of initial reaction rate methods can be found in references 1, 6 and 9.)

The simplest initial reaction rate calculation involves the measurement of the extent of the reaction at a fixed time after initiation of the reaction.[1,6,9] This value is effectively equal to the slope of the linear initial rate curve. It is a popular method because it is conveniently used with flowing streams. Cordos, Crouch and Malmstadt described one of the first computation circuits for the fixed-time method.[75] It consisted of an analogue integration and subtraction network controlled with respect to timing and sequence by a digital logic circuit. This approach yields a very favourable signal-to-noise ratio in the output. Hicks and co-workers[76–78] have also described a similar analogue integration technique but developed a hardware interface system to free their time-shared computer system for control of other automation operations. A completely digital computation system for the fixed-time method has been proposed by Ingle and Crouch[79] which is similar to the analogue operations but employs digital integration. Ingle and Crouch[79] state that the digital method of computation has advantages over the analogue method because there are no drifts and circuit non-linearities, no mechanical and/or analogue switches are necessary, and shorter integration times (faster rates measured) can be employed.

Another commonly used initial reaction rate method is the variable-time (or fixed-concentration) technique[1,6,9,10] in which the time required for the reaction to proceed to a preselected fraction of completion (again, less than 3%) is the measured parameter, which is inversely proportional to the initial reaction rate and concentration of the species being determined. The computation is somewhat more complex than in the fixed-time method. The first completely automated variable-time computation system was based on analogue logic and was developed by Pardue and co-workers.[80,81] Stehl, Margerum and Latterell[82] designed a similar but improved analogue system which eliminated all but one mechanical switch from the circuit. James and Pardue recently reported an analogue variable-time system utilizing tunnel diodes and electronic silicon-controlled diode switches which totally eliminated mechanical switches.[83] This circuit significantly reduced the measurement time intervals that could be determined. Crouch[84] reported the circuit design of a hybrid analogue-digital computation circuit for variable-time systems which eliminated the temperature-sensitive logarithmic analogue operations of the James and Pardue circuit.[83] As analogue systems tend to have significant drift, especially in the integration operation, Pardue, Parker and Willis[85] designed a completely digital computation unit for the variable-time approach. This unit virtually eliminated drift as a source of error in the computation operation and also included a system for noise-averaging, which had not been done in any previous variable-time system.

Some designers have felt that it is more accurate and less susceptible to random error to make a continuous measurement of the total initial-rate curve.[21,23–25,49] As the slope of the initial-rate curve is the parameter that is directly proportional to the concentration of the species of interest, these groups have used analogue (continuous) derivative operations on the initial-rate curves. Weichselbaum and co-workers[21,49] designed a spectrophotometer unit which employed a direct analogue differentiation circuit with filter capacitors to reduce the noise enhancement inherent in direct differentiation of a signal. They also avoided the limited accuracy of analogue logarithmic circuits by using the rate of change of transmittance and the instantaneous value of the transmittance to obtain the derivative of the absorbance (A) with respect to time $[\mathrm{d}(-\log T)/\mathrm{d}t = (-\log e)[(1/T)(\mathrm{d}T/\mathrm{d}t] = \mathrm{d}A/\mathrm{d}t]$. Pardue *et al.* have developed several different systems for the derivative computation technique.[86–88] Instead of direct analogue differentiation, they employed an indirect method for obtaining the slope of the rate curve. Both a servo system[86,87] and an operational amplifier system[88] were used to compare the slope of the initial rate curve with a ramp generated by an operational amplifier integrator. Recently Malmstadt and Crouch[89] critically discussed circuits using manual, mechanical-servo and operational-amplifier slope-matching systems for derivative measurement. In most of these computation units recorders were used to present the response read-out, usually as concentrations. However, Weichselbaum and co-workers[21,49] and Crouch and Malmstadt[90] have shown that the use of digital read-out systems considerably improves the accuracy and precision of rate determinations. Crouch has also discussed the relative merits of direct differentiation and the fixed-time and variable-time methods.[10]

Computation by analogue simulation. Mark, Papa and Reilley[7] and Janata and Mark[25a] have suggested the uses of an analogue simulation approach to the determination of the initial concentration of a reactant. In this approach, the entire reaction rate response curve is simulated with an analogue computer. The initial input voltages to the computer are the electrical analogue of the initial concentrations in the chemical reaction. When the simulated curve exactly matches the experimental reaction rate response curve, the initial unknown concentrations are evaluated from the analogue voltages which yielded the match of the curves. It should be pointed out here that the success of this simulation method rests on an exact knowledge of the reaction mechanisms and rate constants of the reaction being followed.

Computation circuits for simultaneous analysis of mixtures. In recent years considerable research in kinetic methods has been devoted to the simultaneous *in situ* analysis of mixtures.[1,7] As the data reduction of the rate response curves in these differential rate methods is quite complex, built-in computer systems are necessary in order to make these methods practical for routine analytical procedures. Pinkel and Mark,[91] Toren and Davis,[92] and Toren and Gnuse,[93] have reported automatic analogue computer circuits for the solution of the simultaneous equations of the method of proportional equations.[1] Mark, Papa and Reilley,[7] and Janata and Mark[25a] have suggested analogue simulation for solving for initial concentrations in differential rate methods.

Automatic sample handling systems. In spite of the fact that automation of the entire sample handling procedure is an obvious means of eliminating much of the experimental error in sampling, reagent addition, mixing, and timing, and has received considerable attention by the manufacturers of clinical rate-based instrumentation, very little research in this area has been published directly related to kinetic methods of analysis. The most popular automated sampling and mixing systems are based on continuous flow. Various applications and the principles of continuous flow techniques have been discussed in great detail by Blaedel and Hicks,[6] Pardue,[9] Schwartz and Bodansky,[94] in Technicon Instrument Company literature[95] and in the recent reviews by Rechnitz.[14,15] The most recent research publications on automated techniques have generally utilized discrete discontinuous sampling systems, however.[10] Automated injection and refill pipets have been designed by Malmstadt and co-workers.[96,97] Javier, Crouch and Malmstadt have published the design of a completely automated stopped-flow instrument for kinetic analysis,[98] and Deming and Pardue have recently published the design of a computer-controlled electromechanical system for automated reagent addition.[99] Mueller and Burke[100] have reported a real-time computer control system for a reagent-addition unit which would be applicable to kinetic based measurement instrumentation. Fasce and Rej[101] have recently reported an automatic enzyme assay system. Further automated systems which are incorporated in *totally* computer-controlled kinetic analysis instrumentation are also mentioned in the following section. As indicated above, the advertisements and operation manuals of the clinical instrument companies are an excellent source of information on recent advances in automation techniques and hardware. The reader is recommended to contact the sales representatives of the following instrument companies in this regard: Analytical Instrument Division of American Optical Corporation, Richmond, California; Bausch and Lomb Corporation Analytical Systems Division, Rochester, New York; Technicon Company, Incorporated, Tarrytown, New York; Beckman Instrument Corporation, Fullerton, California, and Sherwood Medical Industries, Incorporated, St. Louis, Missouri. A radically new and very effective automated system (ACA) for clinical screening tests has been developed by the Instrument Products Division, E. I. DuPont Company, Wilmington, Delaware. This system employs a separate plastic pack in which each individual test, including the spectrophotometric measurement, is carried out. A computer built into the instrument controls the entire operation.

Sorokin, Gromov, and Chernyskii[102] have described an automated thermochemical apparatus for studying kinetic processes.

Applications of on-line computer systems to kinetic methods of analysis

As the expense of high-speed small digital computer systems goes down, the applications of these small computers as built-in (on-line) units in chemical instrumentation for data reduction, system control, data acquisition, and experimental optimization and design in "real time" have increased sharply. As discussed in an earlier section, the computer was originally used in kinetic methods for on-line fast data acquisition and data reduction to give final display as the concentration of the species in the sample being analysed. The computer was also used in some control applications. However, such limited applications do not efficiently use the full capabilities of the small on-line computer. Recently several research groups have been investigating and developing the small on-line computer for *total* control and operation of the instrumentation in kinetic methods of analysis. Systems have been described in which the computer not only handles the data acquisition and sample-manipulation, but actively takes part in all parts of the experiment by immediate examination of the data in real time and then makes various decisions which optimize the experimental parameters and variables during the actual experiment.[10] It is felt that this is the most important single improvement in kinetic-based analysis, which will greatly expand the routine and specialized applications of the technique.

James and Pardue[103] described an on-line computer system which utilized software to provide the calculations for either fixed-time or variable-time measurements. The signal–time profile is stored in the memory of the computer and the time scale is optimized on the basis of a preliminary rate measurement. This preliminary rate measurement is also used to optimize the time constant of the digital filter system. The basic block diagram of the programme for this system is shown in Fig. 1.

Hicks and co-workers[76–78] used a hybrid analogue-digital approach to on-line computer control. They employed a hardware interface to compute the reaction rate outside the computer, as discussed in an earlier part of this section. The computer was free to monitor and control the electromechanical equipment for the sampling,

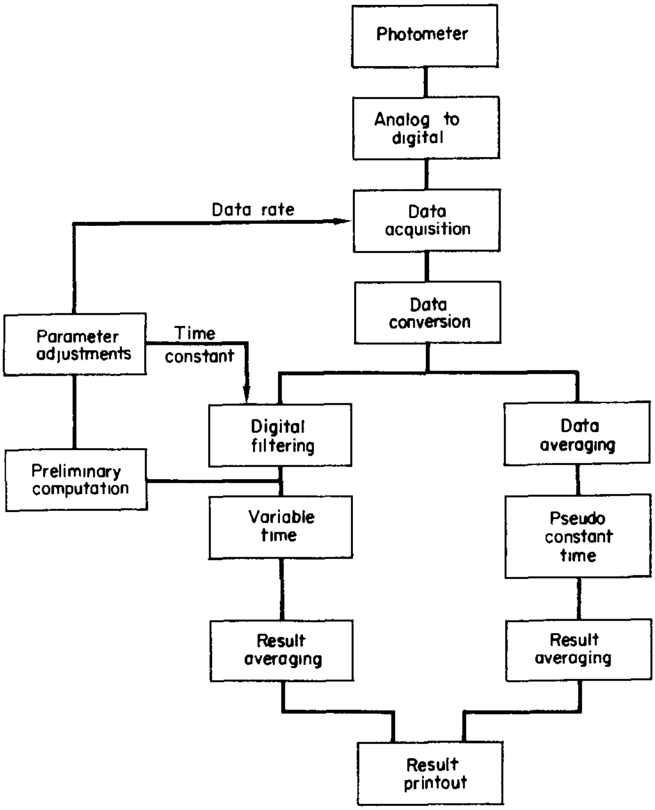


FIG. 1.—Flow diagram of a computer programme for an on-line computerized reaction-rate instrument.[103] Reprinted by permission of the American Chemical Society.

reagent addition, *etc*, for automatic scale selection, calibration, for timing and sequence application, and for output display. A block diagram of this computer system is shown in Fig. 2. Eggert, Hicks and Davis[78] have also discussed use of this hybrid system in experimental control operations.

Recently Willis *et al.*[25] have described the design and characteristics of an on-line computer-controlled stopped-flow system for kinetic analysis. The main feature of this system is its ability to carry out repetitive runs on the same sample and/or do multiple slope measurements on a single reaction for signal-averaging purposes. Such ensemble-averaging results in a very high precision. The programme also provides for display of a variety of kinetic and concentration parameters. Janata and Mark have[104] recently published an extensive discussion of the applications of analogue computer simulation to a wide variety of kinetic, mechanistic and analytical problems.

An excellent discussion of the principles, objectives and general design philosophy of computer-controlled instrumentation for study and characterization of chemical reactions has recently been published by Deming and Pardue.[99] This paper is certainly very important for any researcher interested in computer-based instrument design as it points out clearly the objectives in future design of kinetic analysis instrumentation. In this instrument, routine procedures as well as the decision-making procedures in

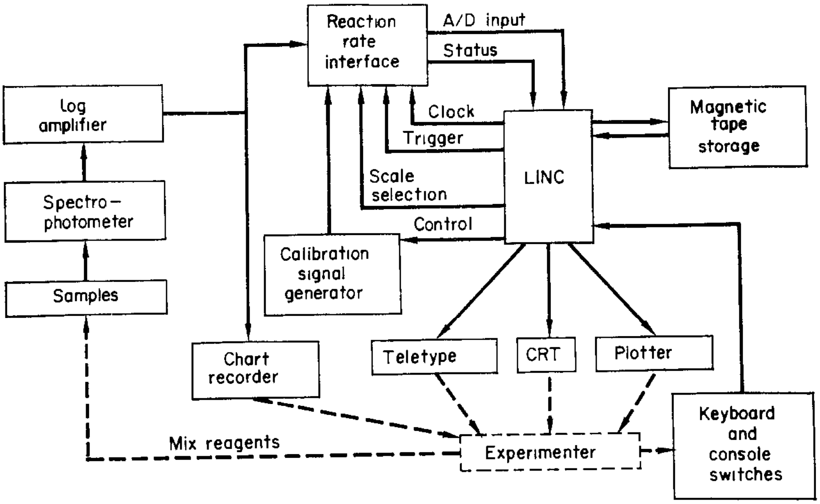


FIG. 2.—Block diagram of a hybrid (interactive) computer system for kinetic analysis.[76] Reprinted by permission of the American Chemical Society.

data interpretation and experimental design have been automated. In this paper, Deming and Pardue presented two very picturesque block diagrams which point out very dramatically the differences in fundamental operational concepts between the procedures conventionally used for the instrumental characterization of a chemical reaction and what these authors conceive as the general future trend of automated reaction characterization.[99] These diagrams are reproduced here as Fig. 3 and 4. This paper also gives the details of the design of such an automated and computerized instrument and the results of test applications are very impressive. There is another

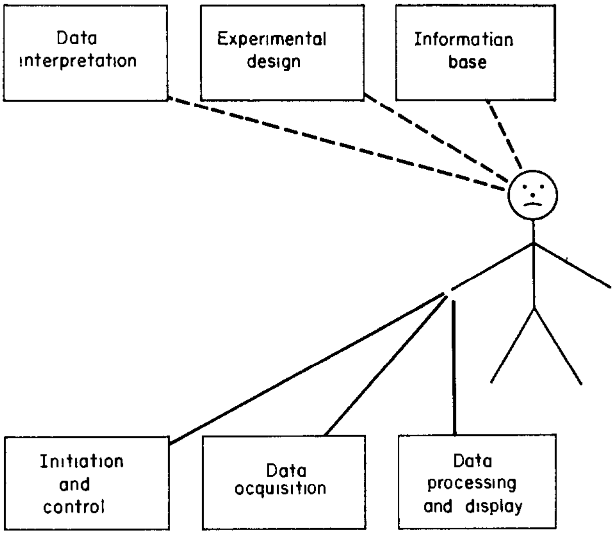


FIG. 3.—Operating procedures in conventional characterization of a chemical reaction.[99] Reprinted by permission of the American Chemical Society.

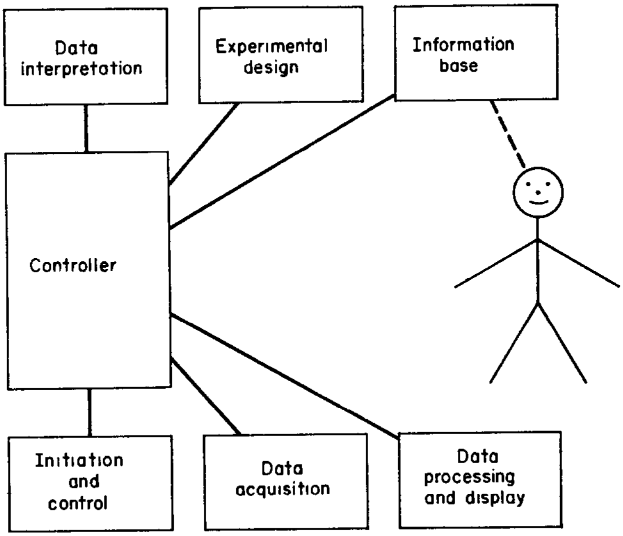


FIG. 4.—Procedures proposed for on-line computerized automated characterization of a chemical reaction.[99] Reprinted by permission of the American Chemical Society.

recent paper on the design and operation of a totally automated chemical instrument system that should be mentioned here, although it does not involve kinetic analysis methods. Perone, Jones and Gutknecht[105] have reported an electroanalytical system which also uses an on-line computer to analyse and interpret the results obtained during a repetitive electrochemical experiment and then control the various experimental parameters of the experiment to optimize the sensitivity and resolution of the response and the analytical results. Perone[106] has also recently published a detailed monograph chapter on the subject of real-time computer applications and optimization of experiments.

BIOLOGICAL AND CLINICAL APPLICATIONS (ENZYME METHODS)

Certainly the greatest amount of both use and research in the field of kinetic-based methods of analysis is in the general area of clinical analysis and other biological applications. Most of this work is oriented towards enzyme assay and the use of enzymes as specific reagents for a variety of different types or classes of reactants, such as the substrate in the enzyme-catalysed conversion reaction, inhibitors, activators, *etc.* As the enzyme is a biological catalyst which acts to lower the activation barrier and hence accelerate the rate of certain specific reactions, without being consumed in the overall conversion reaction and generally without changing the net free energy difference (equilibrium constant) between reactants and products, it is not only logical, but also for the most part necessary, to employ kinetic methods in the complex systems of chemical and biological analysis. As mentioned in the introduction, these types of analysis are of great importance in medical diagnosis and hence so is fundamental research on these analytical techniques, to broaden the scope of application and improve the speed, accuracy and precision of the methods.

Guilbault has recently written a very comprehensive and well-documented book on enzyme methods of analysis.[3] He has also written extensive reviews of recent publications in this field.[14–17] Other recent books by Purdy,[107] Udenfriend,[108] and

Ruyssen and Vandenriesche[109] have extensive discussions of kinetic-based clinical techniques, procedures, and methods. Also, there have been several monograph chapters on the various aspects of the subject by Blaedel and Hicks,[6] Guilbault,[110] Phillips and Elevitch[111] and Pardue.[9] There have also been other review articles by Bergmeyer,[18] Devlin,[19] Roth,[20] Danev[112] and Zuman.[113] It should also be pointed out that the literature of the various enzyme nanufacturers and supply houses as well as that of the various clinical instrumentation manufacturers is a wealth of information on methods and procedures of analysis. The literature will be reviewed here first according to the analytical species being determined and second according to the method used. As the literature is extensive, this review will attempt to cover only reports which represent significant improvements in procedures or inovations and new applications reported in the past few years.

Determination of enzymes

Since the enzyme is a biological catalyst and in most of the enzymatic catalysis reactions is not consumed, the rates of the reactions of the substrate (reactant) are strongly influenced by even small amounts of enzyme present. Thus the rates of enzyme-catalysed reactions are very sensitive to low enzyme concentration. A wide variety of experimental and instrumental procedures and techniques has been employed in enzyme assay.

Spectrophotometric and fluorimetric methods. The instrumental improvements in optical kinetic-based systems have already been discussed in the instrumentation section above. Much of this instrumentation was developed with enzymatic problems in mind.

Using fluorimetric rate-measurements, Guilbault *et al.* have studied the effects of various fluorogenic esters on the determination of cholinesterase.[114] They reported that *N*-methylindoxyl esters were the optimum substrates in terms of both sensitivity and reagent stability. Guilbault and Zimmerman[115] have also reported a technique for the determination of cholinesterase directly on a solid surface. Similarly, Guilbault and Heyn[116] tested several fluorogenic substrates for the determination of cellulase and suggest resorufin butyrate as the best substrate for a *rapid* initial-rate determination. Guilbault and co-workers[117] have developed a considerably more accurate and rapid analysis for hyaluronidase by taking advantage of the high fluorescence efficiency of indigo white. The optimum analytical conditions and fluorogenic substrates for a variety of lipase enzymes have been reported by Guilbault and Sadar[118] and Guilbault and Hieserman.[119] A comparative study of the use of umbelliferone as a fluorogenic substrate for acid and alkaline phosphatase with other commonly used substrates, showed that this substrate increased the sensitivity of the assay by 2–4 orders of magnitude.[120] The applicability of a variety of naphthol derivatives as substrates for the phosphatase enzymes has also been reported.[121–123] A systematic study of several new fluorometric substrates for sulphatase has been made and the fluorimetric method described appears to be superior to the usual colorimetric methods.[119] Fluorometric initial reaction rate methods for amino-acid oxidase,[124] peroxidase,[125] glucose oxidase,[125,126] xanthine oxidase[125] and galactose oxidase[126] have been reported. Guilbault and Kramer[127,128] have described a simple, rapid fluorometric method for the enzymes dehydrogenase, glucose-6-phosphate dehydrogenase, 1,α-glycerophosphate dehydrogenase and glycerol dehydrogenase. Also, an automated procedure for dehydrogenase has been reported which uses the reaction with the substrate resazurin to form the intensely fluorescent resorufin.[17]

A variety of spectrophotometric initial-rate methods for enzyme assay have also been described recently. Most of the methods cited below represent only minor modifications of the established procedures. However, the results reported have been used to show how the accuracy and precision of such determinations can be significantly improved by using modern instrument designs.[10] Weichselbaum and co-workers have reported a very reproducible method for the determination of lactic dehydrogenase.[21,74] These authors[21] and Pardue, Parker and Willis[85] also investigated kinetic methods for alkaline phosphatase. Pardue, Frings and Delaney[80] have reported results for the determination of glucose oxidase and galactose oxidase by a variable-time method. James and Pardue have also studied the analytical results for the determination of alkaline phosphatase by a variable-time procedure[129] and on-line computer system.[103] Toren *et al.*[77] have reported computer-based rate methods for acetic dehydrogenase and alkaline phosphatase.

Electroanalytical methods. The application of electroanalytical techniques to enzyme assay by rate-based methods was introduced less than ten years ago.[17,107] As these techniques are very simple and capable of a high degree of accuracy, electroanalytical methods are quite promising. One of the first methods described was a $\Delta E/\Delta t$ rate method introduced by Guilbault, Kramer and Cannon.[130] This technique has been employed in the determination of cholinesterase,[130] glucose oxidase,[131] xanthine oxidase[132] and peroxide catalase.[133] Potentiometric[58,134,135] and amperometric techniques[65,136,137] have been reported for glucose oxidase and for galactose oxidase.[138] Purdy[139] has reported amperometric and coulometric methods for urinase and urease. Katz[140] has also described a potentiometric method for the determination of urease, using a cation-sensitive electrode system as the detector. Guilbault, Smith and Montalvo[141] have also reported the use of an NH_4^+-selective glass electrode for the determination of deaminase. There have also been polarographic techniques reported for the determination of cholinesterase,[142,143] 3-hydroxyanthranilic oxidase[144] and catalase.[145] Curtin[146] has reported a potentiometric method using a silver–thiol electrode method for cholinesterase. Lipner and co-workers[147] have reported the use of an oxygen galvanic cell system for the analysis of a variety of oxygen-consuming enzymes, and Malmstadt and Piepmeier designed a pH-stat system for a variety of enzyme rate determinations.[148]

Determination of substrates

By far the greatest volume of recent research effort in enzymatic methods of analysis has been in the development of determinations of various substrates of enzyme-catalysed systems. A large variety of both organic and inorganic substrates has been studied. As Guilbault[3,14–16,19] and Bergmeyer[149] have presented extensive compilations of enzymatic methods for substrate analysis, only recent applications will be given here.

Spectrophotometric and fluorometric methods. Several enzymatic methods have recently been reported for the analysis of carbohydrate substrates. Spectrophotometric methods for glucose,[75,80,89] using modifications of the usual glucose oxidase catalysised technique, and galactose[80] by using galactose oxidase have been described by several research groups. Guilbault and co-workers have developed a very useful technique for the fluorimetric analysis of various sugar mixtures.[27,28] They reported the successful determination of lactose, maltose, fructose and glycogen mixtures by first reacting each sugar in separate aliquots with the specific enzyme which converts it into glucose, and using an initial-rate fluorimetric method which follows the formation of resorufin in a coupled reaction to determine the glucose produced. The analysis of several other carbohydrate mixtures, glucose and sorbitol mixtures, and methanol, sorbitol, and xylose mixtures have also been reported.[27,28] Guilbault, Sadar and McQueen[150] have used a similar procedure for the fluorimetric determination of a great variety of organic acids, both for single components of a mixture or for the simultaneous analyses of several acid components of a mixture.

Weichselbaum *et al.*[21] have reported a spectrophotometric maximum rate method for the determination of ammonia and blood urea nitrogen in biological systems. Faway and Dahl,[151] Mondzac, Ehrlich and Seegmiller,[152] Reichelt, Kuamme and Iveit,[153] and Kirsten, Gerz and Kirsten[154] have also described initial rate spectrophotometric methods for ammonia in various biological media. Roch-Ramel[155] and Rubin and Knott[156] have reported fluorimetric methods for the determination of ammonia.

Schulz, Passonneau and Lowry[157] have described a fluorometric method, and Faway, Roth and Faway[158] a spectrophotometric method for inorganic phosphate. Two unique rate methods employing the enzyme catalyst immobilized[17] in a solid matrix have been reported (considerable research is now being carried out on methods of immobilizing enzyme systems without loss of their catalytic activity.)[3,17,59] Hicks and Updike[160] have used lactate dehydrogenase immobilized in a gel for the assay of glucose and lactic acid. They have also coupled an immobilized glucose oxidase system with an electrochemical sensor for the determination of glucose in blood.[161]

Determination of activators

In many enzymatic catalysed reactions a substance called an activator is required before the enzyme itself becomes an active catalyst.[3,17] As the initial reaction rates of such enzymatic systems are proportional to the concentration of the activator (until all the catalyst is activated) rate measurement can be employed to determine the concentration of activator species in the same manner that is used for direct enzyme assay as discussed in another section of this review. Although this application has been shown to have considerable potential[3,6,17] and can under special conditions determine very small amounts [down to 10^{-15} mole (162)], very little research on the analytical applications has been published recently. Only the method for the determination of Mn^{2+} and Mg^{2+} which are activators for isocitric dehydrogenase reactions[6] and the determination of Ca^{2+} and Zn^{2+} activators for alkaline phosphatase[163] have been reported in the last few years.

Determination of inhibitors

There are many substances, called inhibitors, which cause a decrease in the rate of an enzyme-catalysed reaction.[3,6,17] In general, the decrease in the initial rate of an enzymatic reaction is directly proportional to the inhibitor concentration until total inhibition is reached (reaction rate reaches zero). Numerous examples have been reported recently of the determination of most common inorganic anions and cations. Guilbault has compiled a very complete list of the procedures for Ag^+, Al^{3+}, Be^{2+},

Bi^{3+}, Ce^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, In^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, CN^-, $Cr_2O_7^{2-}$, F^- and S^{2-}.[3] Very recently, Townshend and Vaughan have reported the determination of Hg^{2+} and Ag^+ (inhibitors of alcohol dehydrogenase)[164] and Be^{2+} and Zn^{2+} (inhibitors of alkaline phosphatase).[165] With growing concern for the effect of pesticides on the environment and the ecology, there has been considerable research on the application of the selective inhibition of enzyme activity by these substances. Kitz[166] has recently published an extensive review of the inhibition effects on cholinesterase activity, as used for the determination of various organophosphorus compounds. More recently several methods have been reported for a large variety of organophosphorus insecticides, *etc.*[167–174] Methods have been reported for a variety of chlorinated insecticides and herbicides,[171,172,175,176] and carbamate insecticides.[171,172,186–190]

There is a wide variety of factors such as choice of enzyme source and type, substrate, and other reaction conditions, which have considerable effect on the sensitivity and/or selectivity of a reaction for a particular pesticide inhibitor. There have been a large number of studies in this aspect.[180–173,186,189,191,192]

CHEMICAL APPLICATIONS OF RATE METHODS

Comprehensive compilations of the various general chemical applications of kinetic determinations reported before 1969 have been given in two recent books[1,2] and a series of review papers.[11–13,16,183] Druzhinin[184] has reviewed the kinetic-based methods for organic substances, in air-pollution studies. Heil[185] has reviewed kinetic methods applied to water analysis. Thus, this review will list only methods reported during the last two years, except in cases of special importance. These recent publications are listed below in two groups, first the methods for determination of a single species, and second the methods for determination of two or more species by differential reaction rate methods.

Determination of a single component

Inorganic species. The majority of chemical applications of reaction rate methods of analysis have used catalysed reactions and have, in general, employed initial reaction rate procedures. Yatsimirskii has described in detail the techniques and application of catalysed reactions in a recent book.[2]

Klockow, Ludwig and Giraudo[186] have reported the use of a zirconium catalysed reaction between perborate and iodide which can be used for the determination of fluoride. The fluoride acts as an inhibitor in the parts per milliard (ppM) range. Bruton has devised an ion-selective electrode rate method for the determination of both fluoride and chloride.[187] Thompson and Svehla[188] have used the perborate/iodide system for the same type of catalytic determination of iron and molybdenum, and Weisz, Klockow and Ludwig[189] have developed a new electrometric monitoring system for the determination of molybdenum. Cabello-Tomas and West[190] have described a "kineto-chromic" method for trace fluoride determination. Worthington and Pardue have reported a catalytic reaction procedure for the determination of trace ruthenium, using the Ce^{4+} and As^{3+} oxidation-reduction reaction.[191] Janjic, Milovanovic and Celap[192] described a method for the ultramicro determination of manganese by its catalytic action on the oxidation of alizarin by hydrogen peroxide. Analytical applications of the iodine and osmium catalysed reaction between Ce^{4+} and As^{3+} have been discussed by Rodriguez and Pardue.[193] James and Pardue have shown that built-in computer instrumentation is capable of determining levels of 10^{-9}–$10^{-11}M$ osmium, using this reaction system.[103] Kreingol'd and co-workers[194] have described a kinetic method for Cr^{6+} based on the catalysis of oxidation of the herbicide Methurin by potassium bromate. Dolmanova *et al.*[195] also reported a method for Cr^{6+} based on the catalytic oxidation of *o*-dianisidine with hydrogen peroxide. The concentrations of Cu^{2+} solutions have been determined by measuring the effect on the oxidation of furfuraldehyde.[196] Ruthenium has been determined by Ottaway, Fuller and Allan,[197] using the catalysis of the periodate oxidation of the tris[1,10-phenanthroline-iron(II)] complex. Trace determination methods for Ag^+, Hg^{2+} and I^- have been reported by Bognar and Sarosi,[198] based on the catalytic Ag^+–I^- and Hg^{2+}–I^- titrations and the IO_3^-–AsO_3^{3-} Landolt-type indicating system. Lazarev and Lazareva[199,200] have devised two different kinetic methods for V^{5+}. They made use of the catalytic action of V^{5+} on the bromate/5-amino-*N*-phenylanthranilic acid system[199] or the bromate/primary aromatic amine system.[200] Yatsimirskii and Kalinina[201] have also devised a trace vanadium method (0·01–100 ppM) based on the catalytic effect on the iodide oxidation by bromate. Hems, Kirkbright and West[202] have employed the catalytic effect of SO_4^{2-} on the zirconium/Methylthymol Blue reaction, for the determination of sulphate ion. A stopped-flow method for the kinetic determination of Fe^{3+} reacting with thiocyanate ion[23] and Sr^{2+} by a DCTA ligand-exchange reaction have been reported recently.[31]

A method for the determination of trace Cu^{2+} by means of the catalytic effect on the oxidation of amidol by hydrogen peroxide has been reported by Kreingol'd *et al.*[203] Trace methods for the determination of Mn^{2+} by the catalytic effect on the oxidation of Indigo Carmine has been developed by Slychev and Tiginyanu.[204] The Mn^{2+} catalysis of the oxidation of *p*-phenetidine by potassium perchlorate has also been employed in a trace analysis method.[205] A kinetic method for Mn^{2+} has been reported[205] which follows the complexation reaction rate with a sodium carminate–ethylenediamine system, using an integral variant technique. The catalytic effect of iridium on the oxidation of diphenylamines by cerium(IV) has been used in an analytical application by Tikhonova and Yatsimirskii.[207] Yatsimirskii *et al.* have also reported a kinetic method for the determination of iridium, which has been applied to paper chromatographic separation of noble metals.[208] A kinetic method for the determination of cobalt in vitamin B12 uses the catalysis of oxidation of the dye Bordeaux S by hydrogen peroxide.[209] Another catalytic method for Co^{2+} has been reported by Costache and Popa[210] which uses the Bromopyrogallol Red oxidation by peroxide. Filippou, Zyatkovskii and Yatsimirskii have employed the catalysis of the *p*-phenetidine/bromate reaction by Os^{8+} for trace analysis.[211] Segeda[212] has used the Ti^{3+} reaction with hydroxylamine as the basis of a rate method. Bilidiene, Cepelionyte and Jesinskiene[213] have reported a trace Cr^{6+} method based on the catalysis of the Methyl Orange oxidation by hydrogen peroxide. Trace Ag^+ has been determined by means of the catalytic effect on the oxidation of azo dyes by $K_2S_2O_5$.[214] A novel technique for the determination of either Rh^{3+} or Pd^{2+} by catalysis of the reduction of AgBr to Ag in a photographic emulsion by metol–hydroquinone developer has been reported by Pilipenko, Markova and Kaplan.[215]

Several reaction-rate modifications of the classic molybdenum blue method for the determination of inorganic phosphate have been reported.[79,84,98,216,217] These techniques employ either fixed-time or variable-time initial reaction rate measurement.

Similar methods employing the measurement of the initial rates of formation of heteropolymolybdate have been devised by Hargis for the determination of bismuth.[218]

Toropova and co-workers[219] have used an electroanalytical method of measuring the catalytic hydrogen wave of the cobalt–5-sulpho-8-mercaptoquinolinate complex to determine trace amounts of Sb^{3+}. Lukaweiwicz and Fitzgerald[220] have devised a fast photokinetic method for the determination of Fe^{3+}.

Organic species. Gilbert[221] has reported a pulse polarographic method which uses the Co^{2+} catalytic hydrogen wave for determining trace amounts of cystine. Rodziewicz *et al.*[222] have proposed a kinetic method for the determination of various phenolic compounds. A very sensitive method for the estimation of RNA by the Cu^{2+} catalysed orcinol reduction reaction has been reported.[223] Tutt and Schwartz[224] have devised a spectrophotometric assay of Ampicillin (α-aminobenzyl penicillin) involving a maximum rate method. The catalytic polarographic prewave of Ni^{2+} organic diamine systems has been proposed as a means of measuring the pK values of certain sparingly soluble organic amines.[225] A kinetic method for the determination of the stability constants of various metal complexes has been reported by Cohen and Connors.[226] Pillai, Lakshmenon, and Saryanarayana[227] have described a "redoxokinetic" titration method for organic acids. Szepesi and Gorog have reported a method for the determination of organic amines, which follows the rate of the acetylation or formylation reactions.[228]

Simultaneous analysis of mixtures

Inorganic systems. Margerum *et al.*[31] have reported a differential reaction rate method for the analysis of binary and ternary mixtures of lanthanides, transition metals, group II and group III metals, as DCTA complexes reacted with H^+ and/or an exchanging metal ion. Pausch and Margerum[23] have also reported the use of a stopped-flow spectrophotometric method for the simultaneous analysis of binary mixtures of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, using the exchange reactions of Pb^{2+} with alkaline earth metals complexes. Willis *et al.*[24] have improved this method by employing computer control and data reduction. Rodriguez and Pardue[229] have used the iodide and osmium catalysis of the Ce^{4+}–As^{3+} reaction for the simultaneous determination of I^- and Os^{8+}. Ingle and Crouch have reported a simultaneous differential rate procedure for silicate and phosphate in mixtures.[230]

Organic systems. Lohman and Mulligan have analysed mixtures of ethanolamides by a differential saponification rate method.[231] A kinetic method for the analysis of mixtures of glycols, using the cleavage reaction with lead(IV) has been reported by Benson and Fletcher.[232] Binary ketone mixtures have been determined by Toren and Gnuse[93] by taking advantage of the differences in the reaction rates with hydroxyamine hydrochloride. Greinke and Mark[48] have used the same reagent in the determination of various carbonyl mixtures. Zaia, Peruzzo and Plazzogna have reported a differential reaction rate method for mixtures of various hexa-alkyl-ditin compounds.[233] Shresta and Das have reported a second-order graphical extrapolation method for the simultaneous analysis of various organic amine mixtures.[234]

FUNDAMENTAL KINETIC STUDIES RELATED TO ANALYTICAL PROBLEMS

There have been numerous papers in the recent literature concerned with basic or fundamental kinetic studies on chemical systems which are either directly or indirectly related to analytical methods and procedures. Some of the basic work is intended to develop new methods and reactions for kinetic-based analytical techniques and some is intended to determine the mechanism of reactions involved in the more common equilibrium (or thermodynamic) methods. Once the details of such reaction mechanisms are known, it is possible to systematically improve a method. Recent papers in these two catagories are listed below. It should be pointed out that there is a huge volume of literature devoted to both inorganic and organic chemistry which involves the measurement of kinetic characteristics. It has been pointed out previously that this literature is a wealth of potentially analytically useful systems.[1,7] While this review will not attempt to list the publications in this area of research, the reader should be aware of its existence when faced with devising an analytical procedure for a new problem. There are a number of recent reviews of kinetic studies of the reactions of both organic[235–254] and inorganic species.[255–261]

Perhaps one of the major advances in sensors for rapid and selective *in situ* analysis has been the breakthrough in the theory and design of ion-selective electrodes. These have already been employed in a huge number of equilibrium (potentiometric) analytical methods. Recently Rechnitz and co-workers have also demonstrated that ion-selective electrodes are applicable as sensors in kinetic measurements.[60,61,63,64,262–269] They have studied metal complex reactions,[63,64,262,265,266] instrumentation considerations,[61,267] fast reaction applications[268] and biological systems.[60] Friedman, Palaty and Nakashima[270] have used ion-selective glass electrodes in the study of alkali metal ion-exchange processes. Honaker and Freiser[271] and McClellan and Freiser[272] have shown that solvent extraction methods can be employed, under certain conditions, to study the kinetics of fast chelation reactions. Subbaraman, Cordes and Freiser[273] have also studied the affect of auxiliary complexing agents on the rate of Zn^{2+} and Ni^{2+} extraction with diphenythiocarbazone. McClellan and Menis[19] have studied the kinetics and the mechanism of Fe^{2+} extraction with β-isopropyltropolone. Although there have been no direct applications taking advantage of the differential kinetics of extraction processes reported in the recent literature, it is obvious that there is a potential for future development. Hans has published a theoretical paper on electrolyte extraction kinetics.[275]

As the various organic and inorganic forms of phosphate are now recognized as a very large pollution hazard with respect to the ecological balance in natural water systems, the problem of trace determination of phosphates has received considerable attention in the recent literature. The standard colorimetric and/or spectrophotometric method for inorganic phosphate is the reaction with molybdate to form the 12-molybdophosphoric heteropoly acid species. There have been kinetic mechanism studies of these reactions by Javier, Crouch and Malmstadt.[276] In similar kinetic studies which have analytical significance, Hargis and co-workers have studied the reactions for the formation of silicon and bismuth heteropolymolybdates.[218,277–279] Solkovikov and Prinachek have reported the study of the mechanism and kinetics of the reaction of Al^{3+} with hafnium–molybdenum heteropoly acids.[280] Also in the area of environmental problems, Weber and co-workers have reported on studies of the rates of adsorption of organic pollutants,[284] pesticides,[281] and alkylbenzenesulphonates[282,283] on various activated carbons. These studies have potential for the improvement of activated carbon through a better understanding of the adsorption mechanism, and also for the determination and separation of various pesticides and pollutants.[285]

It is important to point out here that another group[286,287] has reported a kinetic-based pollution treatment system based on the *misinterpretation* of the results of Weber and Morris.[282,283]

In the past few years there have been a number of kinetic analytical methods reported that employ ligand-exchange reactions of metal ion complexes. These initial efforts in this area indicate that these types of metal ion complex reaction have considerable promise for broad analytical application, as discussed in a previous section of this review. Because of this potential certain recent papers describing fundamental kinetic and mechanism studies of metal ion complex systems are listed here. Funashashi and Tanaka[288–290] have studied the ligand-exchange reactions of various Co^{2+}, Cu^{2+} and Ni^{2+} complexes with 4-(2-pyridylazo)resorcinol. Frost and Hart have studied the ligand transfer kinetics of reactions of Eu^{3+}–(2,2,6,6-terpyridine) complexes with Tb^{3+}.[291] The kinetics and mechanism of other ligand transfer reactions have also been reported.[292] Ligand-exchange reactions of cobalt complexes have been reported.[293] Carr and Reilley[294] have reported a study on the kinetics of the ligand-exchange reaction of ethylenediaminetetra-acetate ion with ethylenediaminetetra-acetatonickel(II). Pausch and Margerum,[31] and Willis *et al.*[25] have studied the ligand-exchange kinetics of strontium complexes of *trans*-DCTA and hydrogen ion, using Pb^{2+} as a scavenger.

Recently there have been several reports on kinetic studies using thermogravimetric methods. Sharp and Wentworth,[295] Carroll and Manche,[296] and Wentworth and Sharp[297] have had an exchange of correspondence on this subject. Taylor and Watson[298] have reported a method of determining relative reaction rates by a differential thermal analysis method. Cerceo[299] has used an evaporation-rate method to determine the degree of "cure" of polymeric materials. Dorko and co-workers have developed a differential scanning calorimetric method for studying the kinetics of solid state reactions.[300] The application of scanning calorimetry to thermal kinetic studies has been reported by Rogers and Smith.[301] Thermogravimetric studies of decomposition reaction rates have been reported by Savin[302] and reviewed by Sestak[303] and by Skvara and Satava.[304]

Hammer and Craig[305] have studied the kinetics of the β-chloroamine reaction and Joris, Aspila and Chakrabarti[306] have reported the results of the decomposition reactions of monoalkyldithiocarbamates. Sand and Huber have developed a differential constant-current potentiometric method for application to kinetic-based analysis.[307] Frankel[308] has devised a nuclear magnetic resonance technique for following the rates of ion-exchange reactions.

Froede and co-workers[309] have reported the development of a rapid-sampling system for use in studying intermediate-speed reactions. A rapid method for the determination of first-order reaction rate constants has been described by Viale[310] and Roy and Al-Jallo[311] have reported a spectrophotometric study of the kinetics of saponification reactions of alkyl ester compounds. Patton and Langer[312] have reported an interesting reaction kinetic method for the detection of void zones in gas chromatographic columns. Rodriguez and Pardue[230] have made an extensive study of the iodine-catalysed reaction between Ce^{4+} and As^{3+} in sulphuric acid. Other studies of the kinetics of catalysed reactions of potential analytical interest have also been reported. The catalytic effect of Cu^{2+} and Fe^{3+} ions on the reaction of Pu^{3+} with chlorine in chloride solutions has been reported by Mazumdar *et al.*[313]

Habig, Pardue and Worthington[314] have found that the catalysis of the reaction between Ce^{4+} and As^{3+} by Os^{7+} is first-order with respect to Os^{7+} over a wide concentration range. With another osmium-catalysed system, Domka and Marciniec[315] have shown that OsO_4 catalyses the decomposition of hydrogen peroxide and the oxidation of Indigo Carmine with peroxide. Yoshiro and co-workers[316] have reported on the Cu^{+}-catalysed oxidation of Mo^{5+} solutions. The activity of Ag^{+} as a catalyst in the oxidation of Tl^{+} by Ce^{4+} has been studied by Zeltmann.[317] Bhat and Khan[318] have studied the catalytic effects of F^{-} and Cl^{-} on the oxidation reactions of various metal ions.

In other kinetic studies of analytical interest, Burkhart and Newton[319] studied the redox kinetics of V^{2+} and Np^{4+} reactions, Flechon and Chavane[320] studied the reduction of silver salts by EDTA, and Matyakha and co-workers[321] have reported kinetic studies of reduction of Ce^{4+} oxalate complexes by hydrogen peroxide. In other redox reaction studies, Krishna and Singh[322] have reported results on the oxidation of I^{-} by ferricyanide in acid media, Davies and co-workers[323] have reported on the Mn^{2+}–H_2O_2 reaction, and Goldberg and Obukhova[324] have studied Mn^{2+} reduction by caproic acid. Everett and Skoog have made a kinetic study of the As^{3+} and Ce^{4+} redox reaction.[325]

Tockstein and Tocksteinova[326] have developed a unique oxidation-reduction titration which they called a *kinetic titration*. They employed the measurement of the rate of change of potential with time, using a zero faradaic current condition as titrant is continuously added. They report that they were able to determine two substances with exactly the same formal potentials provided the reaction rate constants were different by about two orders of magnitude. Sinfelt has reviewed the applied applications of reaction kinetics and catalytic reactions.[327] Samandi and Jaky have studied the mechanism of the oxidation of various organic carboxylic acids with permanganate.[328] Masood, Shastri and Krishna[329] have studied the effects of the nature and concentration of electrolytes on the kinetics of the alkaline fading of phenolphthalein. Smith[330] has recently published a second edition of the book, *Chemical Engineering Kinetics*, which contains extensive information on applied uses of reaction kinetics and other information of potential analytical interest.

Zusammenfassung—Es wird eine Übersicht über Prinzipien und Anwendung katalytischer und kinetischer Analysenmethoden gegeben.

Résumé—On présente une revue des principes et applications des méthodes d'analyse par catalyse et vitesse de réaction.

REFERENCES

1. H. B. Mark Jr., G. A. Rechnitz and R. A. Greinke, *Kinetics in Analytical Chemistry*, Wiley-Interscience, New York 1968.
2. K. B. Yatsimirskii, *Kinetic Methods of Analysis, Pergamon, Oxford*, 1966.
3. G. G. Guilbault, *Enzymatic Methods of Analysis*, Pergamon, Oxford, 1970.
4. H. V. Bergmeyer, Ed., *Methods of Enzymatic Analysis*, 2nd Ed., Verlag Chimie, Meinheim, 1965.
5. R. Ruyssen and E. L. Vandenriesche, Eds. *Enzymes in Clinical Chemistry*, Elsevier, Amsterdam, 1965.
6. W. J. Blaedel and G. P. Hicks, in *Advances in Analytical Chemistry and Instrumentation*, Vol. 3, C. N. Reilley, Ed., p. 105. Wiley-Interscience, New York, 1964.
7. H. B. Mark, Jr., L. J. Papa, and C. N. Reilley, in *Advances in Analytical Chemistry and Instrumentation*, Vol. 2, C. N. Reilley, Ed., p. 255. Wiley-Interscience, New York, 1963.
8. J. Janata, in *Computers in Chemistry and Instrumentation*. Vol. 3, J. S. Mattson, H. C. MacDonald Jr. and H. B. Mark Jr., Eds., in press. Dekker, New York, 1972.

9. H. L. Pardue in *Advances in Analytical Chemistry and Instrumentation*, Vol. 7, C. N. Reilley and F. W. McLafferty, Eds., p. 141. Wiley-Interscience, New York, 1968.
10. S. R. Crouch in *Computers in Chemistry and Instrumentation*, Vol. 3, J. S. Mattson, H. C. MacDonald Jr. and H. B. Mark Jr., Eds., in press. Dekker, New York, 1972.
11. G. A. Rechnitz, *Anal. Chem.*, 1964, **36**, 453R.
12. *Idem, ibid.*, 1966, **38**, 513R.
13. *Idem, ibid.*, 1968, **40**, 455R.
14. G. G. Guilbault, *ibid.*, 1966, **38**, 527R.
15. *Idem, ibid.*, 1966, **40**, 459R.
16. *Idem, ibid.*, 1970, **42**, 334R.
17. *Idem, Crit. Revs. Anal. Chem.*, 1970, **1**, 377.
18. H. U. Bergmeyer, *Z. Anal. Chem.*, 1965, **211**, 77.
19. T. M. Devlin, *Anal. Chem.*, 1959, **31**, 977.
20. M. Roth, *Methods in Biochem. Anal.*, 1969, **17**, 189.
21. T. E. Weichselbaum, W. H. Plumpe Jr., R. E. Adams, J. C. Hagerty and H. B. Mark Jr., *Anal. Chem.*, 1969, **41**, 725.
22. H. V. Malmstadt and S. R. Crouch, *J. Chem. Educ.*, 1966, **43**, 340
23. D. W. Margerum, J. B. Pausch, G. A. Nysseu and G. F. Smith, *Anal. Chem.*, 1969, **41**, 233.
24. B. G. Willis, W. H. Woodruff, J. R. Frysinger, D. W. Margerum and H. L. Pardue, *ibid.*, 1970, **42**, 1350.
25. B. G. Willis, J. A. Bittikofer, H. L. Pardue and D. W. Margerum, *ibid.*, 1970, **42**, 1340.
25a. J. Janata and H. B. Mark Jr., in *Electroanalytical Chemistry*. Vol. 3, ed. A. J. Bard, p. 1. Dekker, New York, 1968.
26. H. B. Mark Jr., *Anal. Chem.*, 1965, **36**, 1668.
27. G. G. Guilbault, M. H. Sadar and K. Peres, *Anal. Biochem.*, 1969, **31**, 91.
28. G. G. Guilbault and S. H. Sadar, *ibid.*, 1971, in press.
29. T. S. Lee and J. M. Kolthoff, *Ann. Acad. N.Y. Sci.*, 1951, **53**, 1093.
30. R. G. Garmon and C. N. Reilley, *Anal. Chem.*, 1962, **34**, 600.
31. J. B. Pausch and D. W. Margerum, *ibid.*, 1969, **41**, 226.
32. J. D. Roberts and C. Regan, *ibid.*, 1952, **24**, 360.
33. R. A. Greinke and H. B. Mark Jr., *ibid.*, 1966, **38**, 340.
34. S. Siggia and J. G. Hanna, *ibid.*, 1961, **33**, 896.
35. C. N. Reilley and L. J. Papa, *ibid.*, 1962, **34**, 801.
36. L. J. Papa, H. B. Mark Jr. and C. N. Reilley, *ibid.*, 1962, **34**, 1513.
37. E. O. Schmalz and G. Geiseler, *Z. Anal. Chem.*, 1962, **188**, 241.
38. *Idem, ibid.*, 1962, **188**, 253.
39. *Idem, ibid.*, 1962, **190**, 222.
40. *Idem, ibid.*, 1962, **190**, 233.
41. J. D. Ingle Jr. and S. R. Crouch, *Anal. Chem.*, 1971, **43**, 697.
42. H. B. Mark, Jr., R. A. Greinke and L. J. Papa, *Proc. Soc. Anal. Chem. Conf., Nottingham, England*, 1965, p. 490.
43. R. A. Greinke, and H. B. Mark, *Anal. Chem.*, 1966, **38**, 340.
44. *Idem., ibid.*, 1966, **38**, 1001.
45. F. Willeboordse and F. E. Crutchfield, *ibid.*, 1964, **36**, 2270.
46. F. Willeboordse and R. L. Meeker, *ibid.*, 1966, **38**, 859.
47. S. Siggia and J. G. Hanna, *ibid.*, 1964, **36**, 228.
48. R. A. Greinke and H. B. Mark Jr., *ibid.*, 1966, **38**, 1001.
49. T. E. Weichselbaum, W. H. Plumpe Jr. and H. B. Mark Jr., *ibid.*, 1969, 41 (No. 3), 108A.
50. P. A. Loach and R. J. Loyd, *ibid.*, 1966, **38**, 1709.
51. H. L. Pardue and P. A. Rodriguez, *ibid.*, 1967, **39**, 901.
52. H. L. Pardue and S. N. Deming, *ibid.*, 1969, **41**, 986.
53. J. D. Ingle Jr. and S. R. Crouch, *ibid.*, 1971, **43**, 1331.
54. M. L. Franklin, G. Horlick and H. V. Malmstadt, *ibid.*, 1969, **41**, 2.
55. R. B. Johnson, *Clin. Chem* , 1969, **15**, 108.
56. A. Vaughan, G. G. Guilbault and D. Hackney, *Anal. Chem.*, 1971, **43**, 721.
57. R. D. Schroeder, in *Computers in Chemistry and Instrumentation*, Vol. 2, J. S. Mattson, H. C. MacDonald Jr., and H. B. Mark Jr., Eds., p. 259. Dekker, New York, 1972.
58. H. V. Malmstadt and H. L. Pardue, *Anal. Chem.*, 1961, **33**, 1040.
59. M. J. D. Brand and G. A. Rechnitz, *ibid.*, 1970, **42**, 1172.
60. B. Fleet and G. A. Rechnitz, *ibid.*, 1970, **42**, 690.
61. G. A. Rechnitz, *ibid.*, 1969, **41**, (12) 109A.
62. G. A. Rechnitz and T. M. Hseu, *ibid.*, 1969, **41**, 111.
63. G. A. Rechnitz and A. F. Lin, *ibid.*, 1968, **40**, 696.

64. K. Srinavsan and G. A. Rechnitz, *ibid.*, 1968, **40**, 1818.
65. H. L. Pardue, *ibid.*, 1963, **35**, 1240.
66. H. B. Mark Jr. and R. A. Greinke, *J. Chem. Educ.*, 1969, **216**, 869.
67. R. A. Greinke and H. B. Mark Jr., *Anal. Chem.*, 1966, **38**, 390.
68. L. P. Papa, J. H. Paterson, H. B. Mark Jr. and C. N. Reilley, *ibid.*, 1963, **35**, 1889.
69. C. N. Reilley, *J. Chem. Educ.*, 1962, **39**, A853.
70. D. E. Johnson and C. G. Enke, *Anal. Chem.*, 1970, **42**, 329.
71. M. Van Swaay, *J. Chem. Educ.*, 1969, **46**, A515.
72. *Idem*, *ibid.*, 1969, **46**, A565.
73. P. D. Feil, D. G. Kubler and D. J. Wells Jr., *Anal. Chem.*, 1969, **41**, 1908.
74. T. E. Weichselbaum, R. E. Smith and H. B. Mark Jr., *ibid.*, 1969, **41**, 1913
75. E. M. Cordos, S. R. Crouch and H. V. Malmstadt, *ibid.*, 1968, **40**, 1812.
76. G. P. Hicks, A. A. Eggert and E. C. Toren Jr., *ibid.*, 1970, **42**, 729.
77. E. C. Toren Jr., A. A. Eggert, A. E. Sherry and G. P. Hicks, *Clin. Chem.*, 1970, **16**, 215.
78. A. A. Eggert, G. P. Hicks and J. E. Davis, *Anal. Chem.*, 1971, **43**, 736.
79. J. D. Engle Jr. and S. R. Crouch, *ibid.*, 1970, **42**, 1055.
80. H. L. Pardue, C. S. Frings and C. J. Delaney, *ibid.*, 1965, **37**, 1426.
81. H. L. Pardue, M. F. Burke and D. O. Jones, *J. Chem. Educ.*, 1967, **44**, 684.
82. R. H. Stehl, D. W. Margerum and J. J. Latterell, *Anal. Chem.*, 1967, **39**, 1346.
83. G. E. Jamea and H. L. Pardue, *ibid.*, 1968, **40**, 796.
84. S. R. Crouch, *ibid.*, 1969, **41**, 880.
85. H. L. Pardue, R. A. Parker and B. G. Willis, *ibid.*, 1970, **42**, 56.
86. H. L. Pardue, *ibid.*, 1964, **36** 633.
87. *Idem*, *ibid.*, 1969, **36** 1110.
88. H. L. Pardu and W. E. Dahl, *J. Electroanal. Chem.*, 1964, **8**, 268.
89. H. V. Malmstadt and S. R. Crouch, *J. Chem. Educ.*, 1968, **43**, 340.
90. S. R. Crouch and H. V. Malmstadt, *Anal. Chem.*, 1967., **39**, 1090.
91. D. Pinkel and H. B. Mark Jr., *Talanta*, 1965, **12**, 491.
92. E. C. Toren Jr. and J. E. Davis, *Anal. Lett.*, **1**, 289.
93. E. C. Toren Jr. and M. K. Gnuse, *ibid.*, 1968, 1968, **1**, 295.
94. M. K. Schwartz and O. Bodansky, in *Methods of Biochemical Analysis*, Vol. XI, D. Glick, Ed., p. 211. Wiley-Interscience, New York, 1963.
95. Technicon Instrument Company, *Automation in Analytical Chemistry*, Mediad, White Plains, New York, 1967.
96. H. V. Malmstadt and G. P. Hicks, *Anal. Chem.*, 1960, **32**, 445.
97. H. V. Malmstadt and H. L. Pardu, *ibid.*, 1962, **34**, 299.
98. A. C. Javier, S. R. Crouch and H. V. Malmstadt, *ibid.*, 1969, **41**, 239.
99. S. N. Deming and H. L. Pardue, *ibid.*, 1971, **43**, 192.
100. K. A. Mueller and M. F. Burke, *ibid.*, 1971, **43**, 641.
101. C. F. Fasce Jr. and R. Rej, *Clin. Chem.*, 1970, **16**, 972.
102. K. G. Sorokin, M. I. Gromov and A. M. Chernyskii, *Vestn. Akad. Nauk Kaz. SSR*, 1970, **26**, 21.
103. G. E. James and H. L. Pardue, *Anal. Chem.*, 1969, **41**, 1618.
104. J. Janata and H. B. Mark Jr., in *Electroanalytical Chemistry*, Vol. 3, A. J. Bard, Ed., p. 1. Dekker, New York, 1968.
105. S. P. Perone, D. O. Jones and W. F. Gutknecht, *Anal. Chem.*, 1969, **41**, 1154.
106. S. P. Perone, in *Computers in Chemistry and Instrumentation*, Vol. 2, J. S. Mattson, H. C. MacDonald Jr., and H. B. Mark Jr., Eds., p. 423. Dekker, New York, 1972.
107. W. C. Purdy, *Electroanalytical Methods in Biochemistry* McGraw-Hill, New York, 1965.
108. S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, Academic Press, New York, 1962.
109. R. Ruyssen and E. L. Vandenriesche, Eds., *Enzymes in Clinical Chemistry*, Elsevier, Amsterdam, 1965.
110. G. G. Guilbault, in *Fluorescence, Theory, Instrumentation, and Practice*, G. G. Guilbault, Ed., p. 297ff. Dekker, New York, 1967.
111. R. E. Phillips and F. R. Elevitch, in *Progress in Clinical Pathology*, M. Steffani, Ed., p. 62ff. Greene and Stratton, New York, 1966.
112. S. Danev, *Suurem. Med.*, 1970, **21**, 33.
113. P. Zuman, *Methods Enzymol.*, 1969, **16**, 121.
114. G. G. Guilbault, M. H. Sadar, R. Glazer and C. Skoa, *Anal. Lett.*, 1968, **1**, 365.
115. G. G. Guilbault and R. Zimmerman, *ibid.*, 1970, **3**, 133.
116. G. G. Guilbault and A. Heyn, *ibid.*, 1968, **1**, 163.
117. G. G. Guilbault, D. N. Kramer and E. Hackley, *Anal. Biochem.*, 1967, **18** 241.
118. G. G. Guilbault and M. H. Sadar, *Anal. Lett.*, 1968, **1**, 551.
119. G. G. Guilbault and J. Hieserman, *Anal. Chem.*, 1968, **41**, 2006.
120. G. G. Guilbault, M. H. Sadar, R. Glazer and J. Haynes, *Anal. Lett.*, 1968, **1**, 333.

121. G. G. Guilbault and A. Vaughan, *ibid.*, 1970, **3**, 1.
122. R. B. Johnson, *Clin. Chem.*, 1969, **15**, 108.
123. A. Vaughan, G. G. Guilbault and D. Hackney, *Anal. Chem.*, 1971, **43**, 721.
124. G. G. Guilbault and H. Hieserman, *Anal. Biochem.*, 1968, **26**, 1.
125. G. G. Guilbault, P. Brignac and M. Zimmer, *Anal. Chem.*, 1968, **40**, 190.
126. *Idem*, *ibid.*, 1968, **40**, 1256.
127. G. G. Guilbault and D. N. Kramer, *ibid.*, 1964, **36**, 2497.
128. *Idem*, *ibid.*, 1965, **37**, 1219.
129. G. E. James and H. L. Pardue, *ibid.*, 1968, **40**, 796.
130. G. G. Guilbault, D. N. Kramer and P. L. Cannon, *ibid.*, 1962, **34**, 842.
131. G. G. Guilbault, B. Tyson, D. N. Kramer and P. L. Cannon, *ibid.*, 1968, **35**, 582.
132. G. G. Guilbault, D. N. Kramer and P. L. Cannon, *ibid.*, 1964, **36**, 606.
133. G. G. Guilbault, *Anal. Biochem.*, 1966, **41**, 61.
134. H. V. Malmstadt and H. L. Pardue, *Clin. Chem.*, 1962, **8**, 606.
135. H. L. Pardue, R. Simon and H. V. Malmstadt, *Anal. Chem.* 1964, **36**, 735.
136. H. L. Pardue and R. Simon, *Anal. Biochem.*, 1964, **9**, 204.
137. W. J. Blaedel and C. Olsen, *Anal. Chem.*, 1964, **36**, 343.
138. H. L. Pardue and C. Frings *J. Electronal. Chem.*, 1964, **7**, 398.
139. W. C. Purdy, *Anal. Chem.*, 1964, **36**, (No. 4), 29A.
140. S. A. Katz, *ibid.*, 1964, **36**, 2500.
141. G. G. Huilbault, R. K. Smith and J. G. Montalvo Jr., *ibid.*, 1969, **41**, 600.
142. U. Fischerova-Bergerova, *Pracouni Lekavstvi*, 1964, **16**, 111, 8.
143. T. H. Ridgway and H. B. Mark Jr., *Anal. Biochem.*, 1965, **12**, 357.
144. M. N. Gadaleta, E. Lofrumento, C. Landriscina and A. Alifano, *Bull. Soc. Ital. Biol. Sper.*, 1963, **39**, 1866.
145. H. Jacob, *Z. Chem.*, 1964, **4**, 189.
146. C. C. Curtin, *Anal. Biochem.*, 1964, 8, 184.
147. H. Lipner, L. Witherspoon and A. Wahlborg, *Anal. Chem.*, 1965, **37**, 347.
148. H. V. Malmstadt and E. H. Piepmeier, *ibid.*, 1965, **37**, 34.
149. H. V. Bergmeyer, Ed., *Methods in Enzymatic Analysis*, 2nd Ed., Verlag Chemie, Mernheim, 1965.
150. G. G. Guilbault, S. H. Sadar and R. McQueen, *Anal. Chem. Acta*, 1969, **45**, 1.
151. G. Faway and K. Dahl, *Lebanese Med. J.*, 1963, **16**, 169.
152. A. Mondzac, G. Ehrlich and J. Seegmiller, *J. Lab. Clin. Med.*, 1965, **66**, 526.
153. K. L. Reichelt, E. Kjamme and B. Tviet, *Scand. J. Clin. Lab. Invest.*, 1964, **16**, 433.
154. E. Kirsten, C. Gerez and R. Kirsten, *Biochem. Z.*, 1963, **337**, 312.
155. F. Roch-Ramel, *Anal. Biochem.*, 1969, **21**, 372.
156. M. Rubin and L. Knott, *Clin. Chem. Acta*, 1969, **18**, 409.
157. D. W. Schultz, J. V. Passonneau and O. H. Lowry, *Anal. Biochem.*, 1967, **19**, 300.
158. E. Faway, F. Roth and G. Faway, *Biochem. Z.* 1966, **344**, 212.
159. I. Chibata and T. Tosa, *Tompakushitsu Kakusan Koso*, 1966, **11**, 23.
160. G. P. Hicks and S. J. Updike, *Anal. Chem.*, 1966, **38**, 726.
161. S. J. Updike and G. P. Hicks, *Science*, 1967, **158**, 270.
162. O. H. Lowry, V. Passonneau, D. Schulz and M. K. Rock, *J. Biol. Chem.*, 1961, **236**, 2746.
163. A. Townhend and A. Vaughan, *Talanta*, 1970, **17**, 289.
164. *Idem*, *ibid.*, 1970, **17**, 299.
165. *Idem*, *ibid.*, 1969, **16**, 929.
166. R. J. Kitz, *Acta Anaesthes. Scand.*, 1964, **8**, 197.
167. J. Matousek, J. Fischer and J. Cerman, *Chem. Zvesti*, 1968, **22**, 184.
168. S. Saliman, *Ain Shams Sci. Bull.* 1966, **9**, 127.
169. K. Goszezyhska and B. Stycyznska, *Kocz. Panstiu Zukl. Hig.*, 1966, **9**, 127.
169. K. Goszezyhska and B. Stycyznska, *Kocz. Panstiu Zukl. Hig.*, 1968, **19**, 491.
170. G. G. Guilbault, M. H. Sadar and S. Kuan, *Anal. Chim. Acta*, 1972, in press.
171. *Idem*, *ibid.*, 1972, in press.
172. G. G. Guilbault and M. H. Sadar, *J. Agr. Food. Chem.*, 1971, **19**, 357.
173. G. G. Guilbault, S. Kuan and M. H. Sadar, *ibid.*, 1971, **19**, 415.
174. G. G. Guilbault, M. H. Sadar and M. Zimmer, *Anal. Chim. Acta*, 1969, **44**, 361.
175. H. Keller, *Naturwissenschaften*, 1965, **39**, 109.
176. G. G. Guilbault and M. H. Sadar, *Anal. Chem.*, 1969, **41**, 366.
177. M. B. Abou-Donia and D. B. Menzel, *Comp. Biochem. Physiol.*, 1967, **21**, 99.
178. F. Winteringham and K. S. Fowler, *Biochem. J.*, 1966, **99**, 6P.
179. S. Zhuravskaya and T. Bobyreva, *Uzb. Biol. Zh.*, 1968, **12**, 55.
180. G. Voss, *Bull. Environ. Contam. Toxicol.*, 1968, **3**, 339.
181. J. Cohan, R. Dosterbann and F. Berends, *Methods Enzymol.*, 1967, **11**, 686.

182. J. Delga and P. Foulhoux, *Prod. Probl. Pharm.*, 1969, **24**, 184.
183. R. Bontchev, *Talanta*, 1970, **17**, 499.
184. A. A. Druzhinin, *Zh. Uses Khim. Obstichest*, 1970, **15**, 529.
185. G. Heil, *Haus Tech., Essen., Vortragsveroeff*, 1970, **231**, 29.
186. D. Klockow, H. Ludwig and M. A. Giraudo, *Anal. Chem.*, 1970, **42**, 1682.
187. L. G. Bruton, *ibid.*, 1971, **43**, 519.
188. H. I. Thompson and G. Svehla, *Z. Anal. Chem.*, 1969, **247**, 244.
189. H. Weisz, D. Klockow and H. Ludwig, *Talanta*, 1969, **16**, 921.
190. M. L. Cabello-Tomas and T. S. West, *ibid.*, 1969, **16**, 781.
191. J. B. Worthington and H. L. Pardue, *Anal. Chem.*, 1970, **42**, 1157.
192. T. J. Janjic, G. A. Milovanovic and M. B. Celap, *ibid.*, 1970, **42**, 27.
193. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
194. S. Kreingol'd, E. Bozhevol'nov, G. Supin, V. Antonov and A. Panteleimonova, *Zh. Analit. Khim.*, 1969, **24**, 853.
195. I. Dolmanova, G. Zolotova, L. Tarawova and V. Peshkova, *ibid.*, 1969, **24**, 1035.
196. E. Casassas and H. Torres, *Inform. Quim. Anal.*, 1969, **23**, 61.
197. J. Ottaway, C. Fuller, and J. Allan, *Analyst*, 1969, **94**, 1522.
198. J. Bognar and S. Sarosi, *Urikrokhim. Acta*, 1969, 463.
199. A. Lazarev and V. Lazareva, *Zh. Analit. Khim.*, 1969, **24**, 395.
200. *Idem*, *Opred. Midroprimesei*, 1968, **1**, 95.
201. K. B. Yatsimirskii and V. Kalinina, *Zh. Analit. Khim.*, 1969, **24**, 390.
202. R. Hems, G. Kirkbright and T. S. West, *Talanta*, 1969, **16**, 789.
203. S. U. Kreingol'd, E. A. Boxhevol'nov, V. N. Antonova, A. H. Pauteleimonva and L. J. Sosendova, *Otbrytiya, Izobret. Prom. Obraztsy, Tovarnye Znale*, 1970, **47**, 95.
204. Ya. A. Sychev and Ya. D. Tiginyanu, *Zh. Analit. Khim.*, 1969, **24**, 1842.
205. I. F. Dolmantova, V. P. Poddubiendo and V. M. Peshkova, *ibid.*, 1970, **25**, 2146.
206. P. Bartkus, V. Kalesnikaite, and E. Jasinskiene, *Liet TSR Ankst Mokyklu Moksla Darb. Chem. Technol.*, 1969, **10**, 15.
207. L. P. Tikhonova and K. B. Yatsimirski, *Zh. Analit. Khim.*, 1970, **25**, 1766.
208. K. B. Yatsimirskii, L. P. Tikhonova, G. M. Varshal and V. A. Sychkova, *Proc. Anal. Chem. Conf.* 3rd, 1970, **1**, 191.
209. D. Costache and G. Popa, *Rev. Roum. Chim.*, 1970, **15**, 1061.
210. *Idem*, *ibid.*, 1970, **15**, 1349.
211. A. P. Filippov, V. M. Zyatkovskii and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1970, **25**, 1769.
212. A. S. Segeda, *Ukr. Khim. Zh.*, 1970, **36**, 440.
213. E. Bilidiene, J. Cepelionyte and E. Jesinskiene, *Liet TSR Audst, Mokyklu Mokslo Darb, Chem. Chem. Technol.*, 1969, **10**, 55.
214. E. Jasinskiene and N. Roseviante, *Zh. Analit. Khim.*, 1970, **25**, 458.
215. A. T. Pilipenko, L. V. Markova and M. C. Kaplan, *ibid.*, 1970, **25**, 2414.
216. S. Roselowski, *Chem. Analit.* (*Warsaw*), **15**, 157.
217. E. E. Kriss, V. K. Rudenko and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1970, **25**, 1603.
218. L. G. Hargis, *Anal. Chem.*, 1969, **41**, 597.
219. V. Toropova, L. Anisimova, L. Paolichenko and Y. Bankovskii, *Zh. Analit. Khim.*, 1969, **24**, 1031.
220. R. Lukaweiwicz and J. Fitzgerald, *Anal. Lett.*, 1969, **2**, 159.
221. D. D. Gilbert, *Anal. Chim.*, 1969, **41**, 1567.
222. W. Rodziewicz, I. Kwiatkowski, and E. Kwiatkowski, *Chem. Analit.* (*Warsaw*), 1969, **14**, 55.
223. R. I.-San Lin and O. Schjeide, *Anal. Biochem.*, 1969, **27**, 473.
224. D. E. Tutt and M. A. Schwartz, *Anal. Chem.*, 1971, **43**, 338.
225. J. Čaja and H. B. Mark Jr., *ibid.*, 1971, **43**, 964.
226. J. L. Cohen and K. A. Conners, *Am. J. Pharm. Educ.*, 1970, **34**, 197.
227. K. K. J. Pillai, A. S. Lakshmanan and C. V. Suryonarayana, *Electrochim. Acta*, 1970, **15**, 795.
228. G. Szepesi and G. Gorog, *Proc. Anal. Chem. Conf. 3rd*, 1970, **3**, 145.
229. P. A. Rodriguez and H. L. Pardue, *Anal. Chem.*, 1969, **41**, 1369.
230. J. D. Ingle Jr. and S. R. Crouch, *ibid.*, 1971, **43**, 7.
231. F. Lohman and T. Mulligan, *ibid.*, 1969, **41**, 243 .
232. D. Benson and N. Flecher, *Talanta*, 1966, **13**, 1207.
233. P. Zaia, V. Peruzzo and G. Plozzogna, *Anal. Chim. Acta*, 1970, **51**, 317.
234. I. L. Shreste and M. N. Das, *ibid.*, 1970, **50**, 135.
235. Y. Inel, *J. Phys. Chem.*, 1970, **74**, 2581.
236. M. Caplow, *NASA Spec. Publ.* 1968 (publ. 1969), NASA SA 188.
237. I. I. Moiseev, *Kinet. Katal.*, 1970, **11**, 342.
238. T. Ishir, *Kagaka Kogaka*, 1970, **34**, 477.

239. P. C. Moerk, *Kjemi*, 1970, **30**, 9.
240. K. J. Ivin, *Ann. Rept. Progr. Chem., Sect. A*, 1969, **66**, 121.
241. D. A. Leathard and J. H. Purnell, *Ann. Rev. Phys. Chem.*, 1970, **21**, 197.
242. R. Huisgen, *Angew. Chem. Intern. Ed.*, 1970, **9**, 751.
243. J. Hine, *Physical Organic Chemistry*, Holt, New York, 1959.
244. P. D. Bartlett, G. N. Fickes, F. C. Haupt and R. Helgeson, *Accounts Chem. Res.*, 1970, **3**, 117.
245. L. Dorfman, *ibid.*, 1970, **3**, 224.
246. D. S. Tarbell, *ibid.*, 1969, **2**, 296.
247. E. J. Hart, *ibid.*, 1969, **2**, 161.
248. K. U. Ingold, *ibid.*, 1969, **1**, 1.
249. M. Hanack, *ibid.*, 1970, **3**, 209.
250. J. L. Dye, *ibid.*, 1968, **1**, 306.
251. E. J. Kaiser, *ibid.*, 1970, **3**, 145.
252. E. G. Cordes and R. B. Dunlap, *ibid.*, 1969, **2**, 329.
253. G. Modena, *ibid.*, 1971, **4**, 73.
254. K. Yates, *ibid.*, 1971, **4**, 136.
255. D. M. Chizhikov, *Mekh. Kmet. Vosstanov. Metal. Mater. Simp.*, 1968, 15.
256. H. Taube, *Advan. Chem. Ser.*, 1965, **14**, 107.
257. H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.
258. J. Halpern, *ibid.*, 1970, **3**, 386.
259. G. J. Hoytink, *ibid.*, 1969, **2**, 114.
260. J. H. Espenson, *ibid.*, 1970, **3**, 347.
261. R. G. Wilkins, *ibid.*, 1970, **3**, 408.
262. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1968, **40**, 1955.
263. G. A. Rechnitz, *Accounts Chem. Res.*, 1970, **3**, 69.
264. M. J. P. Brand and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1968.
265. T. Hseu and G. A. Rechnitz, *ibid.*, 1968, **40**, 1054.
266. *Idem*, *Anal. Lett.*, 1968, **1**, 629.
267. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1788.
268. *Idem*, *ibid.*, 1969, **41**, 1185.
269. *Idem*, *ibid.*, 1970, **42**, 616.
270. S. Friedman, V. Palaty and M. Nakashima, *Anal. Biochem.*, 1969, **29**, 107.
271. C. B. Honaker and H. Freiser, *J. Phys. Chem.*, 1962, **66**, 127.
272. B. E. McClellan and H. Freiser, *Anal. Chem.*, 1964, **36**, 2262.
273. P. R. Subbaraman, M. Cordes and H. Freiser, *ibid.*, 1969, **41**, 1878.
274. B. E. McClellan and O. Menis, *ibid.*, 1971, **43**, 436.
275. T. Hark, *Union Burma J. Sci. Tech.*, 1968, **1**, 381.
276. A. Javier, S. R. Crouch and A. V. Malmstadt, *Anal. Chem.*, 1969, **41**, 1922.
277. H. D. Goldman and L. G. Hargis, *ibid.*, 1969, **41**, 490.
278. L. G. Hargis, *ibid.*, 1970, **42**, 1494.
279. *Idem*, *ibid.*, 1970, **42**, 1497.
280. E. N. Sokovikov and O. K. Prinachek, *Vestn. Mosk. Univ., Khim.*, 1970, **11**, 367.
281. W. J. Weber Jr. and J. P. Gould in *Organic Pesticides in the Environment, Adv. Chem. Ser.*, 1966, **60**, 280.
282. W. J. Weber Jr. and J. C. Morris, *J. Sanit. Eng. Div.*, 1963, **89**, 31.
283. *Idem*, *ibid.*, 1964, **90**, 79.
284. V. L. Snoeynk and W. J. Weber Jr., in *Adsorption from Aqueous Solution, Adv. Chem. Ser.*, 1968, **79**, 112.
285. J. S. Mattson and H. B. Mark Jr., *Activated Carbon; Surface Chemistry and Adsorption from Solution*, Dekker, New York, 1971.
286. M. W. Zuckerman, *Ph.D. Thesis*, New York University, 1968.
287. M. W. Zuckerman and A. H. Molaf, *J. Water Pollut. Cont. Fed.*, 1970, **42**, 437.
288. S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 763.
289. *Idem*, *ibid.*, 1970, **43**, 769.
290. *Idem*, *Inorg. Chem.*, 1969, **8**, 2159.
291. G. H. Frost and F. A. Hart, *J. Chem. Soc. D*, 1970, 836.
292. I. I. Kalinchenko and E. N. Yurchenko, *Spektrosk. Fr. Sib Soveshch, 4th*, 1965, (Publ. 1969), 182.
293. M. J. Hynes, G. D. Dewit and D. A. Sweigart, *Inorg. Chem.*, 1971, **10**, 196.
294. J. D. Carr and C. N. Reilley, *Anal. Chem.*, 1970, **42**, 51.
295. J. H. Sharp and S. A. Wentworth, *ibid.*, 1969, **41**, 2060.
296. B. Carroll and P. Manche, *ibid.*, 1970, **42**, 1296.
297. S. A. Wentworth and J. H. Sharp, *ibid.*, 1970, **92**, 1297.

298. L. J. Taylor and S. W. Watson, *ibid.*, 1970, **42**, 297.
299. E. Cerceo, *ibid.*, 1969, **41**, 191.
300. E. A. Dorko, A. S. Hughes and C. R. Downs, *ibid.*, 1970, **42**, 253.
301. R. N. Rogers and L. C. Smith, *Thermochimica Acta*, 1970, **1**, 1.
302. V. O. Savin, *Zh. Fiz. Khim.*, 1970, **44**, 1046.
303. J. Sestek, *Chem. Listy*, 1970, **64**, 695.
304. F. Skvara and V. Safava, *J. Therm. Anal.*, 1970, **2**, 325.
305. C. F. Hammer and J. A. Graig, *Anal. Chem.*, 1970, **42**, 1588.
306. S. J. Joris, K. L. Aspila and C. L. Chakrabarti, *ibid.*, 1970, **42**, 647.
307. J. R. Sand and C. O. Huber, *ibid.*, 1970, **42**, 238.
308. J. S. Frankel, *ibid.*, 1970, **42**, 1638.
309. H. C. Froede, J. Cowan, T. W. Reid and I. B. Wilson, *ibid.*, 1970, **42**, 1209.
310. R. O. Viale, *ibid.*, 1970, **42**, 1834.
311. R. Roy and H. Al-Jallo, *ibid.*, 1969, **41**, 1725.
312. J. E. Patton and S. H. Langer, *ibid.*, 1970, **42**, 1449.
313. A. Mazumdar, R. Gupta and P. Natarajun, *U.S. At. Energy Comm.*, *Rept.* AETT 275, 1967.
314. R. Habig, H. L. Pardue and J. Worthington, *Anal. Chem.*, 1967, **39**, 600.
315. F. Domka and B. Marciniec, *Chem. Analit.* (*Warsaw*), 1969, **14**, 145.
316. Y. Yoshiro, T. Takeuchi, A. Kinoshita and S. Uchida, *Bull. Chem. Soc. Japan*, 1968, **41**, 765.
317. E. Zeltman, *Diss. Abst. B*, 1967, **28**, 1815.
318. T. Bhat and I. Khan, *J. Less-Common Metals*, 1968, **14**, 240.
319. M. Burkhart and T. Newton, *J. Phys. Chem.*, 1969, **44**, 1741.
320. J. Flechon and F. Chavane, *Bull. Soc. Chim. France*, 1968, 3143.
321. V. Matyakha, V. Milov, N. Kroty and P. Pernimov, *Zh. Neorgan. Khim.*, 1967, **12**, 3331.
322. B. Krisha and H. Singh, *Chim. Anal.* (*Paris*), 1967, **49**, 330.
323. G. Davis, L. Krischenbaum and K. Kristin, *Inorg. Chem.*, 1968, **7**, 146.
324. V. M. Goldberg and L. K. Obukhova, *Vestn. Akad. Nauk USSR*, 1967, **43**, 88.
325. K. G. Everett and D. A. Skeog, *Anal. Chem.*, 1971, **43**, 1541.
326. A. Tockstein and D. Tocksteinova, *Collection Czech. Chem. Commun.*, 1969, **34**, 1625.
327. J. H. Sinfelt, *Ind. Eng. Chem.*, 1970, **62**, 22.
328. L. Samandi and M. Jaky, *Tetrahedron Lett.*, 1970, **40**, 3489.
329. A. Masood, N. K. Shastri, and K. Krishna, *Chim. Anal. Paris*, 1970, **52**, 1289.
330. J. M. Smith, *Chemical Engineering Kinetics*, 2nd Ed., McGraw-Hill, New York, 1970.

Talanta, 1972, Vol. 19, pp. 717 to 746. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

REACTION RATE METHODS IN ANALYSIS

HARRY B. MARK, JR.
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, U.S.A.

(*Received* 22 *June* 1971. *Accepted* 30 *October* 1971)

Summary—A review is given of the principles and application of catalytic and reaction rate methods of analysis.

AS INSTRUMENTATION technology, measurement techniques, electronic circuitry, and analytical procedures have advanced in recent years to a very high degree of development, the accuracy and precision necessary to make dynamic reaction systems applicable to both routine and special analytical problems have become available. Thus, there has been considerable research by a fairly large number of analytical chemists on the development of instrumentation, methods, and applications of kinetic (dynamic) based analyses for both new and old analytical problems. In fact, some analytical chemists, the author included, have been heard to say that these advances in instrumentation and electronic circuitry have "opened up a completely *new* area of research in analytical chemistry." Such a statement is not really accurate, of course, as kinetic based methods of analysis have been used for many years by clinical chemists for enzyme assay and other biological and medical tests. It would be more correct to say that analytical chemists have recently realized the tremendous potential in the application of kinetic methods and are now opening up new areas and applications for these methods. Also they are actively engaged in improving the sensitivity as well as the accuracy and precision of such methods. This realization of the potential of kinetics in analysis came about when it was recognized that kinetic based procedures have several inherent properties which can be used advantageously in analysis.

First, analytical chemists have long realized that in a real analytical problem, the species to be determined is rarely found unaccompanied by one or more substances that are closely related chemically and/or physically, and generally separation techniques must be used, which are often laborious and lead to considerable error in the analysis. There are also cases, such as the analysis of the ratio of different functional groups in the same polymer molecules, where non-destructive separation is impossible. Thus, it is clear that the analysis should (or must) be performed without prior separation.

Methods for *in situ* analysis of a mixture of species having similar properties can be classified as either thermodynamic (equilibrium) or kinetic (dynamic) depending on the method used to eliminate or reduce the interference of the other components of the mixture. A thermodynamic masking involves the alteration of the equilibrium conditions of the solution in such a way as to render all reactions, except the one(s) of analytical interest, thermodynamically unfavoured. The kinetic approach involves

---

* For reprints of this Review, see Publisher's announcement near the end of the issue.

utilizing differences in the reaction rates (or adjusting them if necessary) to isolate the reactions(s) of analytical interest. The thermodynamic differences in reactions of closely related compounds, such as homologues or isomers, with a common reagent are often much too small to be used for analysis of mixtures. However, the kinetic differences are usually quite large and permit either individual or simultaneous *in situ* analysis of the components of the mixture. This arises from the fact that the free energy of activation and hence the rate constant for any reaction is very dependent on the effect of structure of the reactants on formation of the activated complex, *etc.* Thus, reactions of closely related species which differ slightly in structure will often have essentially the same net change in free energy for the overall reaction but will reach equilibrium at widely varying rates. Also, changes in temperature, solvent characteristics, activity changes, *etc.*, have much larger effects on the relative rate constants of similar species than they do on the relative values of the equilibrium constants.

Secondly, a large number of inorganic and organic reactions can now be used in analysis. Many chemical reactions are not sufficiently uniform in behaviour to be used in equilibrium-based methods as they attain equilibrium slowly, have side-reactions, or are not sufficiently quantitative (the formation constants are too small) to be applicable. However, the same reactions can be used easily under initial reaction-rate conditions (explained below in the text). Also catalytic kinetic methods are considerably more sensitive than equilibrium methods, and kinetic-based enzymatic reactions are often extremely selective for a particular substrate.

On the other hand, kinetic techniques have one obvious and serious disadvantage. Any dynamic measurement includes time as an experimental variable, which is not the case in equilibrium measurement. It is probably this consideration that has made analytical chemists in the past somewhat afraid of using kinetics as an analytical tool. However, recent developments in instrumentation, especially in computer-based data analysis, signal-averaging and automation have overcome this fear of lower measurement accuracy.

As a result of this increase in interest, several books have been recently published on various aspects of the subject.[1–5] Mark, Rechnitz and Greinke[1] published a comprehensive text on kinetic analytical techniques and mechanistic studies related to analysis problems, Yatsimirskii[2] has given an extensive compilation and discussion of the application of catalytic reactions in trace analysis, and Guilbault,[3] Bergmeyer,[4] and Ruyssen and Vandenriesche[5] have written texts covering the area of enzymatic reactions in analysis. There have also been monograph chapters by Blaedel and Hicks,[6] Mark, Papa and Reilley,[7] Janata,[8] Pardue[9] and Crouch[10] on various aspects of kinetic analysis. The last two are especially significant as they deal with the principles and advances in instrumentation designed *specifically* for kinetic analysis, There have also been the extensive review articles by Rechnitz,[11–13] Guilbault,[14–17] Bergmeyer,[18] Devlin[19] and Roth[20] on various aspects of kinetic analysis in chemistry and clinical chemistry.

Because the early literature on reaction rate techniques applied to chemical analysis is very well reviewed in the publications cited, this review will generally cover only the literature contributions of the past 2–5 years, though particularly important earlier work will be cited.

The topics reviewed individually are recent advances in methods of kinetic analysis, new procedures and approaches to chemical analysis, and reports of kinetic studies of systems which are of specific interest and/or application to analysis. (The huge literature concerned with fundamental kinetic studies of reaction kinetics and mechanisms will not be reviewed.)

MATHEMATICAL BASIS OF KINETIC METHODS OF ANALYSES

A very large number of methods for the calculation of the initial concentration(s) of the species of interest from reaction rate data have been developed over the past few years. These methods involve, in general, simple mathematical manipulation and rearrangement of the usual differential or integral forms of the classical reaction rate equations. With few exceptions most have been reported within the past 5—10 years. They can be classified in two main categories: methods for a single species and methods for the simultaneous *in situ* analysis of mixtures. Within each category, the methods can be subdivided according to the kinetic order of the reactions: pseudo zero-order or initial rate methods, first-order and pseudo first-order methods, and second-order techniques. The principles, mathematical treatments, applicability and limitations of these methods have been discussed in some of the works already cited.[1,6,7,9,10] Recent papers are reviewed below.

Methods for determination of a single species

Pseudo zero-order methods. This approach is the most commonly used in routine and special applications, partly owing to the simplicity of the calculations and the fact that essentially all catalytic methods, both chemical and enzymatic, use pseudo zero-order conditions during the rate measurement. The principle of the initial-rate methods is simple as they are based on taking measurements only during the initial 1–3% or so of total reaction. Under these conditions the amount of reactant consumed and product formed is negligible (*i.e.*, the concentration of the reactants does not change appreciably during the period of the rate measurement) and hence the rate curve is essentially linear, its slope being proportional to the concentration of the reactant being determined.[1,6,7,9,10] There are other advantages besides simplicity of calculation. First , the reverse reaction can be ignored, and secondly, complications such as side-reactions are minimal. Three initial-rate methods are described in the literature. The direct approach is the derivative slope method where the rate of the reaction is measured by electronic derivative circuitry.[9,10,21,22] Margerum and co-workers[23–25] have described a stopped-flow derivative method for determination of a single species. This technique uses repetitive slope measurement during each run, and signal-averaging by a built-in computer to improve the analytical results. In the second approach, essentially a two-point method called the fixed-time method,[1,6,7,9,10] the change in concentration of product (output signal) is measured over a fixed time-interval, giving ($\Delta C/\Delta t$) which is, of course, the slope of the rate curve. The third approach is also a two-point method, the variable-time method.[1,6,7,9,10] In this method the time interval, Δt, required for the output signal to vary between two fixed values (ΔC) is measured. These three initial reaction rate methods have been used for both catalysed and uncatalysed reactions.[1,6,9] The concentrations of the catalyst (including enzymes) as well as of catalyst activators and inhibitors have been determined.[1,3,9,17]

First-order and pseudo first-order methods. Crouch has discussed the principles and parameters of importance for a non-linear response variable-time procedure for first-order and pseudo first-order reactions.[10] Mark, Rechnitz and Greinke[1] have also discussed the criteria for neglecting the contributions of either faster or slower-reacting components in the kinetic determination of a single species in a mixture. Janata and Mark[25a] have suggested analogue simulation techniques for the analysis of such rate curves.

Second-order methods. Very little work has been reported on the analytical applications of second-order conditions for determination of a single species. Weichselbaum *et al.*[21] have described derivative methods in which the maximum rate observed during an autocatalysed reaction run under second-order conditions was applicable for the determination of ammonia and blood-urea nitrogen. Janata and Mark[25a] have also discussed analogue simulation of second-order rate curves for determination of initial concentrations.

Methods for the simultaneous in situ *analysis of mixtures*

The development of methods for the *in situ* simultaneous determination of closely related components of mixtures has received considerable attention. As discussed in the instrumentation section, the tremendous advances in the accuracy and precision of rate measurements makes these methods practical.

Pseudo zero-order methods. Mark has reported an initial reaction rate method for the simultaneous assay of two alcohols, using enzyme-catalysed reactions.[26] Guilbault and co-workers[17,27,28] have reported a very effective method for the *in situ* analysis of multicomponent mixtures of a large variety of different and closely related substrates by taking advantage of enzyme catalysis selectivity.

First-order and pseudo first-order methods. Though each of the methods developed for reactions of this type is applicable to true first-order reactions, all the applications reported, with the exception of radionuclide decay reactions, are to second-order reactions run under pseudo first-order conditions (where either the reactants or the reagents are in very large excess and, hence, do not change appreciably in concentration during the course of the reaction).[1] A graphical method (called the logarithmic extrapolation method) based on the extrapolation of a typical first-order log response *vs.* time plot of the total rate curve has been described for binary mixtures where the reagent is in large excess with respect to the total concentration of the unknown in the mixture.[1] Lee and Kolthoff have described a mathematical single-point method based on a single measurement made at a fixed time during the reaction, for the same pseudo first-order conditions.[29] Garmon and Reilley have described a very simple and successful method of proportional equations based on the principle of constant fractional life.[1,7,30] This method is applicable to both simple and complex first-order reaction sequences. Margerum and co-workers[23–25,31] have described a continuous measurement approach to the method of proportional equations which is more accurate than the finite point approach of Garmon and Reilley[1,30] and have extended the method successfully to three-component mixtures. Roberts and Regan[32] have devised a mathematical single-point rate measurement procedure and Greinke and Mark[33] have devised a method of proportional equations for the reaction condition which is pseudo first-order with respect to the reagent concentration ($[\text{reagent}] \ll [\text{mixture}]$).

Second-order methods. Siggia and Hanna[34] have devised a second-order graphical (logarithmic) extrapolation procedure for the complete analysis of binary mixtures, the reagent and reactant concentrations being of the same order of magnitude. Reilley and Papa developed a second-order linear extrapolation method for the special case where [mixture] = [reagent].[35] For both of these second-order systems Reilley and Papa[35] and Papa, Mark and Reilley[36] have developed mathematical single-point and double-point methods which eliminate the need for a graphical plot. Lee and Kolthoff[29] have developed a different mathematical single-point method for the special case [mixture] = [reagent]. Schmalz and Geiseler[37–40] have reported a graphical differential method and graphical integral method for second-order reactions. They have presented several different modifications of each method.

Applicability and limitations of the various methods for the analysis of mixtures. As can be seen above, many different methods have been reported in recent years. These methods not only employ different reaction order conditions, but also use different mathematical and/or graphical methods of data manipulation and display and some make certain experimental and mathematical assumptions. The choice of the best method and conditions for a specific problem is not intuitively obvious,[1] and considerable work on this problem has recently been reported. Ingle and Crouch have examined the relative merits and limitations of the fixed-time and variable-time methods of data treatment for catalytic and pseudo first-order reaction procedures.[41] They have shown that the fixed-time method is preferable for first- or pseudo first-order reactions and substrate determinations in catalytic reactions. However, their error analysis shows that the variable-time approach is best for enzyme and catalyst determinations and also for non-linear response-rate curves. Reilley and Papa[35] and Papa, Mark and Reilley[36] have discussed the optimum conditions for the second-order linear and graphical extrapolation methods. Mark, Greinke and co-workers[1,36,42,43] have developed a very detailed error analysis for all the first-order and pseudo first-order methods discussed above. They have shown that for binary mixtures the choice of the best method for a particular mixture and of the optimum analysis conditions and experimental parameters of the chosen method was strongly dependent on the ratio of the rate constants as well as on the ratio of the initial concentrations of the species of interest in the mixture. They also gave a set of rules of thumb[1,42] for use as rapid guide lines for the choice of method and optimum conditions. There have also been a few experimental comparisons of the results obtained by using some of the pseudo first-order methods,[1,44–46] which are in general agreement with the theoretical predictions of the error analysis treatments. Siggia and Hanna[47] and Greinke and Mark[48] have also discussed the relative influence of synergistic effects on the accuracy of the various first-order and pseudo first-order methods. Such effects can often be ignored in graphical extrapolation methods, but can lead to huge errors in any of the non-graphical methods. Greinke and Mark[48] point out that when a non-graphical method is used it is absolutely necessary to have a very complete understanding of all the chemistry of the reactions employed.

Recently there has been a very important series of papers by Margerum and co-workers on the parameters affecting the accuracy of the simultaneous analysis of mixtures by pseudo first-order reaction methods.[23–25,31] Their conclusions are that their approach to the problem is the superior method in several examples of the use of reaction rate methods for analysis. In the early development of differential reaction rate methods for the simultaneous *in situ* analysis of mixtures of closely related substances, the chemical reactions used were not suitable for continuous automatic measurement of the entire rate response curves,[1,7] and calculations were generally done by hand. Hence, the emphasis at that time in the development of the reaction rate methods was on minimizing the number of experimental points taken and on predetermining the optimum times, *etc.*, for taking the readings.[1,7] However, in recent years the advances in electronic circuitry and computer technology have had a tremendous influence on the design of instrumentation for kinetic analysis. These instrumental advances have also had a strong influence on the principles and approaches to differential rate methods. Margerum and co-workers[23–25,31] (and also Weichselbaum and co-workers[21,49]) have shown conclusively that the use of built-in computation systems allows continuous analysis of the entire reaction rate curve. The results are thus immediately processed with both ensemble averaging and smoothing routines. Experimental results and detailed error analysis have shown that this approach to data acquisition, reduction and display leads to a much greater accuracy and precision of the analytical results.[23–25,31] In fact, good results can be obtained for fast reaction differential rate analyses where the usual finite or minimal data point methods fail completely.[23,31] Obviously, this approach will be that used in most future developments in kinetic-based methods of analysis.

INSTRUMENTATION

As mentioned above, the major reason for the considerable increase in practical applications of kinetic-based methods is the tremendous advance that has been made in quantitative chemical instrumentation and electronics in the past few years, especially the efforts of instrument manufacturers and certain research groups to design instruments which apply these technological advances to meet the special features and demands of kinetic measurements on dynamic systems. Perhaps the most important of these advances is a consequence of the fantastic developments in both analogue and digital computer technology, as a result of which low-cost linear and digital integrated circuits have been made readily available to people interested in designing chemical instrumentation for ultrasensitive measurement. To quote a statement in a recent publication by Crouch,[10] the availability of integrated circuits "is revolutionizing instrumentation in science."

The instrumental advances can be classified in three separate but overlapping categories. First there are the improvements in the accuracy and precision of the reaction monitoring system electronics such as the excitation and transducer response circuits which create and measure the signal which is proportional to some time-dependent parameter in the chemical reaction (*e.g.*, improved stabilization of spectrophotometer light sources and increases in the sensitivity of photoelectric transducer circuitry). Secondly, the availability of low-cost computing elements has made it possible to build into the instruments either limited or elaborate self-contained computing capability. The extent and elaboration of the computation capability is, of course, reflected in the price of the instrument. These built-in computers can vary from a simple device to convert an initial-rate slope into a digital display of the concentration of the species to be determined, to a full-scale computing device which not only handles data reduction but also controls the operation and timing of the sequencial operations in the experiment. In the extreme case, the computing device operates in a feed-back mode and can sample and analyse results during the course of an experiment and then alter the experimental control parameters in such a way as to optimize the sensitivity and/or selectivity of the determination. The third area of advance is in automation design. This includes advances in the mechanical design and accuracy of sampling units, reagent addition and mixing procedures, *etc*, as well as the application of computing devices to start, control and time the automated procedures and devices (which illustrates the overlap of the three categories).

In the area of new developments in instrumentation of kinetic methods of analysis, there have been two excellent monograph chapters published recently which discuss the basic principles and applications of analogue–digital circuitry employed in considerable detail data reduction and automation design.[9,10] The chapter by Crouch[10] is especially comprehensive and clear in its discussion of computer-based kinetic method instrumentation.

Reaction monitoring

System electronic circuitry. The first problem in improving the accuracy and precision of kinetic-based analytical results is improving the quantitative nature of the total reaction monitoring system (spectrophotometric, potentiostatic, conductometric, *etc.*) and modifying it specifically for time-dependent measurements in following reaction rates. It is convenient to discuss the advances according to the type of measurement system.

Spectrophotometric systems. One of the major problems in adapting spectrophotometric instrumentation to kinetic measurement is that of light-source variation. This problem is inherent in any spectrophotometric system and even though this technique is relatively simple and generally applicable, it has caused kineticists in the past to shy away from spectrophotometric systems for accurate measurement, because such light-fluctuations are often of the same or similar time period as the reaction being followed.[21,49] Most commercial spectrophotometers which are designed for time-independent spectral measurements minimize such light-source variations by the use of double-beam optical systems which partially cancel fluctuations by periodic comparison of reference and sample beam intensities. Such double-beam systems have not generally been considered suitable for spectrophotometric instruments specifically designed for reaction rate measurement. Such systems seriously limit the response-time of the instrument, tend to introduce significant noise, and also add to the cost and complexity of the instrument,[10,21,49] so most designs for kinetics instrumentation employ a single-beam (non-wavelength-scanning) system and concentrate on lamp stabilization.

Weichselbaum and co-workers[21,49] have described a simple stabilization system which regulates the lamp voltage. This circuit compensates for variations in the lamp filament resistance and is thus more efficient than the more common techniques which regulate only the applied voltage or the applied current. Further stabilization is achieved by having a thermal convection baffle in the lamp housing. This source system was reported to give a drift of less than 0·003 absorbance units per hour.

As the stabilization method of Weichselbaum *et al.*[21,49] controls the lamp electrical input and does not directly control the actual lamp output intensity, an uncertainty is introduced into the measurement. Loach and Loyd,[50] and Pardue and co-workers[51,52] have reported several different circuits which use an optical feed-back system for lamp stabilization. The lamp output beam is split and one beam is monitored by means of a photomultiplier tube, the signal from which is fed back to the lamp power supply as an error signal which modifies the power supply voltage to maintain a constant intensity output. Fluctuation of less than 0·03% transmission per hour has been attained.[50]

The elimination of detector noise and drift is also a critical problem in the application of a spectrophotometric system to kinetic analysis, especially if the derivative of the rate curve is being determined by a built-in computation module or unit[21,49] as discussed in a later section. Weichselbaum and co-workers[21,49] discussed the relative signal-to-noise ratios for photodiode tubes and photomultiplier tubes in some detail. They found that when both types of phototransducer are operated at the same anode current, the photodiode tube has a higher signal-to-noise ratio than the photomultiplier. They concluded that the photodiode tube was thus more applicable in non-wavelength-scanning spectrometers designed for kinetic measurement, where light source intensity is not a limiting factor. Crouch and co-workers[10,53] have pointed out correctly that this evaluation of comparative applicability from signal-to-noise ratios at constant anode current is not valid for all spectrophotometric uses. They demonstrated that for systems where the light level is low and/or cannot be controlled, a photomultiplier gives better results. Weichselbaum and co-workers[21,49] have also reported that vacuum phototubes have more favourable signal-to-noise ratios than similar gas-filled tubes. A recent paper by Franklin, Horlick and Malmstadt[54] discusses the optimum criteria for stability of the power supply to the detector.

Recently, fluorimetric methods for kinetic analysis of a variety of materials, mainly of a biological nature, have also been developed.[10,55,56] This technique, although less general in application, has inherent advantages over normal absorbance spectrophotometry in that it is considerably more sensitive for certain high-efficiency fluorescent systems, and in dilute solution the fluorescence intensity is directly proportional to chemical concentration, which reduces signal processing (linearization) significantly. Though so far no papers have been published specifically describing special electronic circuit design and modification of standard fluorimeters for kinetic measurement, it can be stated that similar criteria and/or requirements for detector noise and drift and excitation light-source reproducibility are the same as discussed above for spectrophotometric measurements.

Electrometric systems. Because of the simplicity and ease of making highly accurate current or voltage measurements (made possible by analogue operational amplifier circuitry[57]) considerable work has recently been done on adaptation of potentiometric, constant-current coulometric, and amperometric monitoring of reaction rates for analytical determinations. Some of the early work on potentiometric measurement used a concentration cell technique.[58] Rechnitz and co-workers[59–64] have described the applications of various ion-selective electrodes in potentiometric measurement of reaction rates and kinetic analysis. They have also reported the application of a fast-response, high input-impedance, differential amplifier circuit for kinetic measurement, using two different ion-selective electrodes as the potentiometric cell.[59] Janata and Mark have suggested the application of constant-current coulometric techniques for simultaneous differential reaction rate analysis.[25a] Pardue has described the application of a polarized rotating platinum electrode system using amperometric detection for kinetic-based determinations.[65]

Conductometric instrumentation based on operational amplifier circuitry has also been described for use in kinetic methods of analysis.[66–69] Recently a bipolar-pulse modification of conductometric measurement has been described by Johnson and Enke.[70] This technique seems to be very promising for rate measurement because of its great sensitivity to small changes in conductance.

Reaction temperature control apparatus. As essentially all chemical reaction rates are very strongly dependent on temperature, considerable effort has been made to design simple but highly reliable thermostatic reaction cells and convenient but accurate temperature control systems (generally water-baths). A very comprehensive discussion of the design and construction of temperature control systems has been given by Van Swaay.[71,72]

Pardue and Rodriguez[51] designed a spectrophotometer cell which was sealed into a Lucite outer jacket which allowed water from a thermostatic bath to be in direct contact with the spectrophotometer cell walls. This permitted rapid temperature equilibration of the reactant solutions mixed by stirring in the cell. Weichselbaum and co-workers[21,49] described a spectrophotometer cell which had a separate mixing chamber above the cell itself. Both compartments were thermostatically controlled and the mixing chamber was fitted with an effective magnetic induction stirrer. Very rapid temperature equilibration on mixing of reagents was reported. Feil *et al.*[73] have reported a rapid temperature equilibration cell specifically designed for use with the Beckman DU spectrophotometer. Excellent temperature regulation (±0·005° at 25°) was attained.

Weichselbaum, Smith and Mark[74] described a proportional dual thermistor bridge temperature-control system using analogue–digital control circuitry. With use of the jacketed cell described above,[21,49] better than ±0·01° regulation in the cell was attained at various temperatures. The system was designed so that four different controlled temperatures (15°, 25°, 30°, and 37°) could be attained automatically in a few minutes by simply pushing a selector switch.

Data reduction and display systems

In the application of kinetic methods to routine analysis the detector signal response being used to follow the course of the chemical reaction must be converted into some convenient form, ideally directly into the concentration of the species being determined. Consequently a large volume of research on this has been reported. Systems described vary from the very simple to virtually a built-in digital computer unit.

Computation systems for initial reaction rate methods. Most practical reaction rate based procedures (enzymatic and other clinical assay methods in particular) measure only the initial 1–3% of the overall reaction rate curve, primarily because the mechanism and hence the kinetics are well-behaved in the early stages and the initial rate is essentially constant (pseudo zero-order) with time over this period and is directly proportional to the concentration of the species to be determined. (Detailed discussions of the theory and principles of initial reaction rate methods can be found in references 1, 6 and 9.)

The simplest initial reaction rate calculation involves the measurement of the extent of the reaction at a fixed time after initiation of the reaction.[1,6,9] This value is effectively equal to the slope of the linear initial rate curve. It is a popular method because it is conveniently used with flowing streams. Cordos, Crouch and Malmstadt described one of the first computation circuits for the fixed-time method.[75] It consisted of an analogue integration and subtraction network controlled with respect to timing and sequence by a digital logic circuit. This approach yields a very favourable signal-to-noise ratio in the output. Hicks and co-workers[76–78] have also described a similar analogue integration technique but developed a hardware interface system to free their time-shared computer system for control of other automation operations. A completely digital computation system for the fixed-time method has been proposed by Ingle and Crouch[79] which is similar to the analogue operations but employs digital integration. Ingle and Crouch[79] state that the digital method of computation has advantages over the analogue method because there are no drifts and circuit non-linearities, no mechanical and/or analogue switches are necessary, and shorter integration times (faster rates measured) can be employed.

Another commonly used initial reaction rate method is the variable-time (or fixed-concentration) technique[1,6,9,10] in which the time required for the reaction to proceed to a preselected fraction of completion (again, less than 3%) is the measured parameter, which is inversely proportional to the initial reaction rate and concentration of the species being determined. The computation is somewhat more complex than in the fixed-time method. The first completely automated variable-time computation system was based on analogue logic and was developed by Pardue and co-workers.[80,81] Stehl, Margerum and Latterell[82] designed a similar but improved analogue system which eliminated all but one mechanical switch from the circuit. James and Pardue recently reported an analogue variable-time system utilizing tunnel diodes and electronic silicon-controlled diode switches which totally eliminated mechanical switches.[83] This circuit significantly reduced the measurement time intervals that could be determined. Crouch[84] reported the circuit design of a hybrid analogue-digital computation circuit for variable-time systems which eliminated the temperature-sensitive logarithmic analogue operations of the James and Pardue circuit.[83] As analogue systems tend to have significant drift, especially in the integration operation, Pardue, Parker and Willis[85] designed a completely digital computation unit for the variable-time approach. This unit virtually eliminated drift as a source of error in the computation operation and also included a system for noise-averaging, which had not been done in any previous variable-time system.

Some designers have felt that it is more accurate and less susceptible to random error to make a continuous measurement of the total initial-rate curve.[21,23–25,49] As the slope of the initial-rate curve is the parameter that is directly proportional to the concentration of the species of interest, these groups have used analogue (continuous) derivative operations on the initial-rate curves. Weichselbaum and co-workers[21,49] designed a spectrophotometer unit which employed a direct analogue differentiation circuit with filter capacitors to reduce the noise enhancement inherent in direct differentiation of a signal. They also avoided the limited accuracy of analogue logarithmic circuits by using the rate of change of transmittance and the instantaneous value of the transmittance to obtain the derivative of the absorbance (A) with respect to time $[\mathrm{d}(-\log T)/\mathrm{d}t = (-\log e)[(1/T)(\mathrm{d}T/\mathrm{d}t] = \mathrm{d}A/\mathrm{d}t]$. Pardue *et al.* have developed several different systems for the derivative computation technique.[86–88] Instead of direct analogue differentiation, they employed an indirect method for obtaining the slope of the rate curve. Both a servo system[86,87] and an operational amplifier system[88] were used to compare the slope of the initial rate curve with a ramp generated by an operational amplifier integrator. Recently Malmstadt and Crouch[89] critically discussed circuits using manual, mechanical-servo and operational-amplifier slope-matching systems for derivative measurement. In most of these computation units recorders were used to present the response read-out, usually as concentrations. However, Weichselbaum and co-workers[21,49] and Crouch and Malmstadt[90] have shown that the use of digital read-out systems considerably improves the accuracy and precision of rate determinations. Crouch has also discussed the relative merits of direct differentiation and the fixed-time and variable-time methods.[10]

Computation by analogue simulation. Mark, Papa and Reilley[7] and Janata and Mark[25a] have suggested the uses of an analogue simulation approach to the determination of the initial concentration of a reactant. In this approach, the entire reaction rate response curve is simulated with an analogue computer. The initial input voltages to the computer are the electrical analogue of the initial concentrations in the chemical reaction. When the simulated curve exactly matches the experimental reaction rate response curve, the initial unknown concentrations are evaluated from the analogue voltages which yielded the match of the curves. It should be pointed out here that the success of this simulation method rests on an exact knowledge of the reaction mechanisms and rate constants of the reaction being followed.

Computation circuits for simultaneous analysis of mixtures. In recent years considerable research in kinetic methods has been devoted to the simultaneous *in situ* analysis of mixtures.[1,7] As the data reduction of the rate response curves in these differential rate methods is quite complex, built-in computer systems are necessary in order to make these methods practical for routine analytical procedures. Pinkel and Mark,[91] Toren and Davis,[92] and Toren and Gnuse,[93] have reported automatic analogue computer circuits for the solution of the simultaneous equations of the method of proportional equations.[1] Mark, Papa and Reilley,[7] and Janata and Mark[25a] have suggested analogue simulation for solving for initial concentrations in differential rate methods.

Automatic sample handling systems. In spite of the fact that automation of the entire sample handling procedure is an obvious means of eliminating much of the experimental error in sampling, reagent addition, mixing, and timing, and has received considerable attention by the manufacturers of clinical rate-based instrumentation, very little research in this area has been published directly related to kinetic methods of analysis. The most popular automated sampling and mixing systems are based on continuous flow. Various applications and the principles of continuous flow techniques have been discussed in great detail by Blaedel and Hicks,[6] Pardue,[9] Schwartz and Bodansky,[94] in Technicon Instrument Company literature[95] and in the recent reviews by Rechnitz.[14,15] The most recent research publications on automated techniques have generally utilized discrete discontinuous sampling systems, however.[10] Automated injection and refill pipets have been designed by Malmstadt and co-workers.[96,97] Javier, Crouch and Malmstadt have published the design of a completely automated stopped-flow instrument for kinetic analysis,[98] and Deming and Pardue have recently published the design of a computer-controlled electromechanical system for automated reagent addition.[99] Mueller and Burke[100] have reported a real-time computer control system for a reagent-addition unit which would be applicable to kinetic based measurement instrumentation. Fasce and Rej[101] have recently reported an automatic enzyme assay system. Further automated systems which are incorporated in *totally* computer-controlled kinetic analysis instrumentation are also mentioned in the following section. As indicated above, the advertisements and operation manuals of the clinical instrument companies are an excellent source of information on recent advances in automation techniques and hardware. The reader is recommended to contact the sales representatives of the following instrument companies in this regard: Analytical Instrument Division of American Optical Corporation, Richmond, California; Bausch and Lomb Corporation Analytical Systems Division, Rochester, New York; Technicon Company, Incorporated, Tarrytown, New York; Beckman Instrument Corporation, Fullerton, California, and Sherwood Medical Industries, Incorporated, St. Louis, Missouri. A radically new and very effective automated system (ACA) for clinical screening tests has been developed by the Instrument Products Division, E. I. DuPont Company, Wilmington, Delaware. This system employs a separate plastic pack in which each individual test, including the spectrophotometric measurement, is carried out. A computer built into the instrument controls the entire operation.

Sorokin, Gromov, and Chernyskii[102] have described an automated thermochemical apparatus for studying kinetic processes.

Applications of on-line computer systems to kinetic methods of analysis

As the expense of high-speed small digital computer systems goes down, the applications of these small computers as built-in (on-line) units in chemical instrumentation for data reduction, system control, data acquisition, and experimental optimization and design in "real time" have increased sharply. As discussed in an earlier section, the computer was originally used in kinetic methods for on-line fast data acquisition and data reduction to give final display as the concentration of the species in the sample being analysed. The computer was also used in some control applications. However, such limited applications do not efficiently use the full capabilities of the small on-line computer. Recently several research groups have been investigating and developing the small on-line computer for *total* control and operation of the instrumentation in kinetic methods of analysis. Systems have been described in which the computer not only handles the data acquisition and sample-manipulation, but actively takes part in all parts of the experiment by immediate examination of the data in real time and then makes various decisions which optimize the experimental parameters and variables during the actual experiment.[10] It is felt that this is the most important single improvement in kinetic-based analysis, which will greatly expand the routine and specialized applications of the technique.

James and Pardue[103] described an on-line computer system which utilized software to provide the calculations for either fixed-time or variable-time measurements. The signal–time profile is stored in the memory of the computer and the time scale is optimized on the basis of a preliminary rate measurement. This preliminary rate measurement is also used to optimize the time constant of the digital filter system. The basic block diagram of the programme for this system is shown in Fig. 1.

Hicks and co-workers[76–78] used a hybrid analogue-digital approach to on-line computer control. They employed a hardware interface to compute the reaction rate outside the computer, as discussed in an earlier part of this section. The computer was free to monitor and control the electromechanical equipment for the sampling,

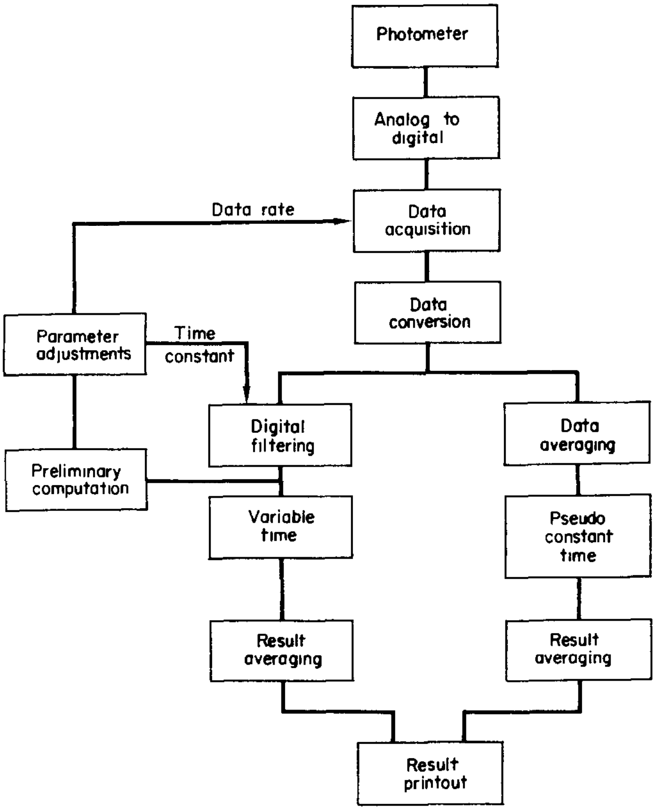


FIG. 1.—Flow diagram of a computer programme for an on-line computerized reaction-rate instrument.[103] Reprinted by permission of the American Chemical Society.

reagent addition, *etc*, for automatic scale selection, calibration, for timing and sequence application, and for output display. A block diagram of this computer system is shown in Fig. 2. Eggert, Hicks and Davis[78] have also discussed use of this hybrid system in experimental control operations.

Recently Willis *et al.*[25] have described the design and characteristics of an on-line computer-controlled stopped-flow system for kinetic analysis. The main feature of this system is its ability to carry out repetitive runs on the same sample and/or do multiple slope measurements on a single reaction for signal-averaging purposes. Such ensemble-averaging results in a very high precision. The programme also provides for display of a variety of kinetic and concentration parameters. Janata and Mark have[104] recently published an extensive discussion of the applications of analogue computer simulation to a wide variety of kinetic, mechanistic and analytical problems.

An excellent discussion of the principles, objectives and general design philosophy of computer-controlled instrumentation for study and characterization of chemical reactions has recently been published by Deming and Pardue.[99] This paper is certainly very important for any researcher interested in computer-based instrument design as it points out clearly the objectives in future design of kinetic analysis instrumentation. In this instrument, routine procedures as well as the decision-making procedures in

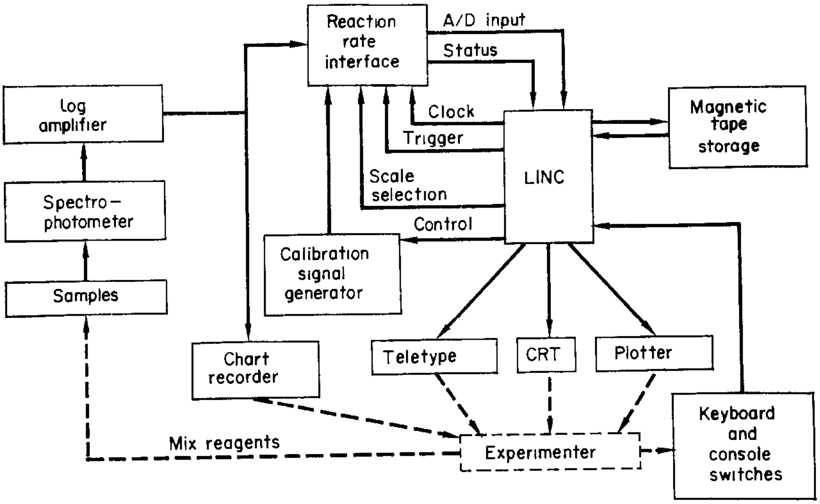


FIG. 2.—Block diagram of a hybrid (interactive) computer system for kinetic analysis.[76] Reprinted by permission of the American Chemical Society.

data interpretation and experimental design have been automated. In this paper, Deming and Pardue presented two very picturesque block diagrams which point out very dramatically the differences in fundamental operational concepts between the procedures conventionally used for the instrumental characterization of a chemical reaction and what these authors conceive as the general future trend of automated reaction characterization.[99] These diagrams are reproduced here as Fig. 3 and 4. This paper also gives the details of the design of such an automated and computerized instrument and the results of test applications are very impressive. There is another

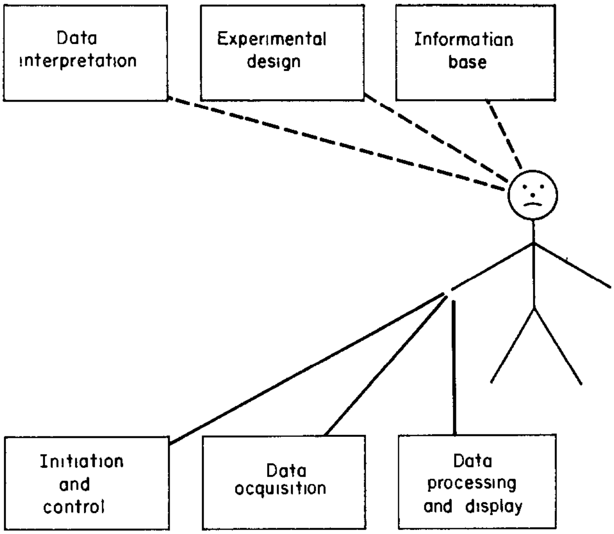


FIG. 3.—Operating procedures in conventional characterization of a chemical reaction.[99] Reprinted by permission of the American Chemical Society.

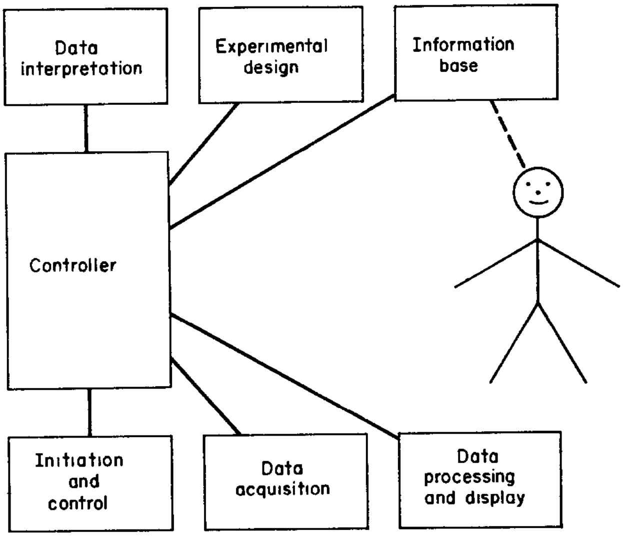


FIG. 4.—Procedures proposed for on-line computerized automated characterization of a chemical reaction.[99] Reprinted by permission of the American Chemical Society.

recent paper on the design and operation of a totally automated chemical instrument system that should be mentioned here, although it does not involve kinetic analysis methods. Perone, Jones and Gutknecht[105] have reported an electroanalytical system which also uses an on-line computer to analyse and interpret the results obtained during a repetitive electrochemical experiment and then control the various experimental parameters of the experiment to optimize the sensitivity and resolution of the response and the analytical results. Perone[106] has also recently published a detailed monograph chapter on the subject of real-time computer applications and optimization of experiments.

BIOLOGICAL AND CLINICAL APPLICATIONS (ENZYME METHODS)

Certainly the greatest amount of both use and research in the field of kinetic-based methods of analysis is in the general area of clinical analysis and other biological applications. Most of this work is oriented towards enzyme assay and the use of enzymes as specific reagents for a variety of different types or classes of reactants, such as the substrate in the enzyme-catalysed conversion reaction, inhibitors, activators, *etc.* As the enzyme is a biological catalyst which acts to lower the activation barrier and hence accelerate the rate of certain specific reactions, without being consumed in the overall conversion reaction and generally without changing the net free energy difference (equilibrium constant) between reactants and products, it is not only logical, but also for the most part necessary, to employ kinetic methods in the complex systems of chemical and biological analysis. As mentioned in the introduction, these types of analysis are of great importance in medical diagnosis and hence so is fundamental research on these analytical techniques, to broaden the scope of application and improve the speed, accuracy and precision of the methods.

Guilbault has recently written a very comprehensive and well-documented book on enzyme methods of analysis.[3] He has also written extensive reviews of recent publications in this field.[14–17] Other recent books by Purdy,[107] Udenfriend,[108] and

Ruyssen and Vandenriesche[109] have extensive discussions of kinetic-based clinical techniques, procedures, and methods. Also, there have been several monograph chapters on the various aspects of the subject by Blaedel and Hicks,[6] Guilbault,[110] Phillips and Elevitch[111] and Pardue.[9] There have also been other review articles by Bergmeyer,[18] Devlin,[19] Roth,[20] Danev[112] and Zuman.[113] It should also be pointed out that the literature of the various enzyme nanufacturers and supply houses as well as that of the various clinical instrumentation manufacturers is a wealth of information on methods and procedures of analysis. The literature will be reviewed here first according to the analytical species being determined and second according to the method used. As the literature is extensive, this review will attempt to cover only reports which represent significant improvements in procedures or inovations and new applications reported in the past few years.

Determination of enzymes

Since the enzyme is a biological catalyst and in most of the enzymatic catalysis reactions is not consumed, the rates of the reactions of the substrate (reactant) are strongly influenced by even small amounts of enzyme present. Thus the rates of enzyme-catalysed reactions are very sensitive to low enzyme concentration. A wide variety of experimental and instrumental procedures and techniques has been employed in enzyme assay.

Spectrophotometric and fluorimetric methods. The instrumental improvements in optical kinetic-based systems have already been discussed in the instrumentation section above. Much of this instrumentation was developed with enzymatic problems in mind.

Using fluorimetric rate-measurements, Guilbault *et al.* have studied the effects of various fluorogenic esters on the determination of cholinesterase.[114] They reported that *N*-methylindoxyl esters were the optimum substrates in terms of both sensitivity and reagent stability. Guilbault and Zimmerman[115] have also reported a technique for the determination of cholinesterase directly on a solid surface. Similarly, Guilbault and Heyn[116] tested several fluorogenic substrates for the determination of cellulase and suggest resorufin butyrate as the best substrate for a *rapid* initial-rate determination. Guilbault and co-workers[117] have developed a considerably more accurate and rapid analysis for hyaluronidase by taking advantage of the high fluorescence efficiency of indigo white. The optimum analytical conditions and fluorogenic substrates for a variety of lipase enzymes have been reported by Guilbault and Sadar[118] and Guilbault and Hieserman.[119] A comparative study of the use of umbelliferone as a fluorogenic substrate for acid and alkaline phosphatase with other commonly used substrates, showed that this substrate increased the sensitivity of the assay by 2–4 orders of magnitude.[120] The applicability of a variety of naphthol derivatives as substrates for the phosphatase enzymes has also been reported.[121–123] A systematic study of several new fluorometric substrates for sulphatase has been made and the fluorimetric method described appears to be superior to the usual colorimetric methods.[119] Fluorometric initial reaction rate methods for amino-acid oxidase,[124] peroxidase,[125] glucose oxidase,[125,126] xanthine oxidase[125] and galactose oxidase[126] have been reported. Guilbault and Kramer[127,128] have described a simple, rapid fluorometric method for the enzymes dehydrogenase, glucose-6-phosphate dehydrogenase, 1,α-glycerophosphate dehydrogenase and glycerol dehydrogenase. Also, an automated procedure for dehydrogenase has been reported which uses the reaction with the substrate resazurin to form the intensely fluorescent resorufin.[17]

A variety of spectrophotometric initial-rate methods for enzyme assay have also been described recently. Most of the methods cited below represent only minor modifications of the established procedures. However, the results reported have been used to show how the accuracy and precision of such determinations can be significantly improved by using modern instrument designs.[10] Weichselbaum and co-workers have reported a very reproducible method for the determination of lactic dehydrogenase.[21,74] These authors[21] and Pardue, Parker and Willis[85] also investigated kinetic methods for alkaline phosphatase. Pardue, Frings and Delaney[80] have reported results for the determination of glucose oxidase and galactose oxidase by a variable-time method. James and Pardue have also studied the analytical results for the determination of alkaline phosphatase by a variable-time procedure[129] and on-line computer system.[103] Toren *et al.*[77] have reported computer-based rate methods for acetic dehydrogenase and alkaline phosphatase.

Electroanalytical methods. The application of electroanalytical techniques to enzyme assay by rate-based methods was introduced less than ten years ago.[17,107] As these techniques are very simple and capable of a high degree of accuracy, electroanalytical methods are quite promising. One of the first methods described was a $\Delta E/\Delta t$ rate method introduced by Guilbault, Kramer and Cannon.[130] This technique has been employed in the determination of cholinesterase,[130] glucose oxidase,[131] xanthine oxidase[132] and peroxide catalase.[133] Potentiometric[58,134,135] and amperometric techniques[65,136,137] have been reported for glucose oxidase and for galactose oxidase.[138] Purdy[139] has reported amperometric and coulometric methods for urinase and urease. Katz[140] has also described a potentiometric method for the determination of urease, using a cation-sensitive electrode system as the detector. Guilbault, Smith and Montalvo[141] have also reported the use of an $NH_4{}^+$-selective glass electrode for the determination of deaminase. There have also been polarographic techniques reported for the determination of cholinesterase,[142,143] 3-hydroxyanthranilic oxidase[144] and catalase.[145] Curtin[146] has reported a potentiometric method using a silver–thiol electrode method for cholinesterase. Lipner and co-workers[147] have reported the use of an oxygen galvanic cell system for the analysis of a variety of oxygen-consuming enzymes, and Malmstadt and Piepmeier designed a pH-stat system for a variety of enzyme rate determinations.[148]

Determination of substrates

By far the greatest volume of recent research effort in enzymatic methods of analysis has been in the development of determinations of various substrates of enzyme-catalysed systems. A large variety of both organic and inorganic substrates has been studied. As Guilbault[3,14–16,19] and Bergmeyer[149] have presented extensive compilations of enzymatic methods for substrate analysis, only recent applications will be given here.

Spectrophotometric and fluorometric methods. Several enzymatic methods have recently been reported for the analysis of carbohydrate substrates. Spectrophotometric methods for glucose,[75,80,89] using modifications of the usual glucose oxidase catalysised technique, and galactose[80] by using galactose oxidase have been described by several research groups. Guilbault and co-workers have developed a very useful technique for the fluorimetric analysis of various sugar mixtures.[27,28] They reported the successful determination of lactose, maltose, fructose and glycogen mixtures by first reacting each sugar in separate aliquots with the specific enzyme which converts it into glucose, and using an initial-rate fluorimetric method which follows the formation of resorufin in a coupled reaction to determine the glucose produced. The analysis of several other carbohydrate mixtures, glucose and sorbitol mixtures, and methanol, sorbitol, and xylose mixtures have also been reported.[27,28] Guilbault, Sadar and McQueen[150] have used a similar procedure for the fluorimetric determination of a great variety of organic acids, both for single components of a mixture or for the simultaneous analyses of several acid components of a mixture.

Weichselbaum *et al.*[21] have reported a spectrophotometric maximum rate method for the determination of ammonia and blood urea nitrogen in biological systems. Faway and Dahl,[151] Mondzac, Ehrlich and Seegmiller,[152] Reichelt, Kuamme and Iveit,[153] and Kirsten, Gerz and Kirsten[154] have also described initial rate spectrophotometric methods for ammonia in various biological media. Roch-Ramel[155] and Rubin and Knott[156] have reported fluorimetric methods for the determination of ammonia.

Schulz, Passonneau and Lowry[157] have described a fluorometric method, and Faway, Roth and Faway[158] a spectrophotometric method for inorganic phosphate. Two unique rate methods employing the enzyme catalyst immobilized[17] in a solid matrix have been reported (considerable research is now being carried out on methods of immobilizing enzyme systems without loss of their catalytic activity.)[3,17,59] Hicks and Updike[160] have used lactate dehydrogenase immobilized in a gel for the assay of glucose and lactic acid. They have also coupled an immobilized glucose oxidase system with an electrochemical sensor for the determination of glucose in blood.[161]

Determination of activators

In many enzymatic catalysed reactions a substance called an activator is required before the enzyme itself becomes an active catalyst.[3,17] As the initial reaction rates of such enzymatic systems are proportional to the concentration of the activator (until all the catalyst is activated) rate measurement can be employed to determine the concentration of activator species in the same manner that is used for direct enzyme assay as discussed in another section of this review. Although this application has been shown to have considerable potential[3,6,17] and can under special conditions determine very small amounts [down to 10^{-15} mole (162)], very little research on the analytical applications has been published recently. Only the method for the determination of Mn^{2+} and Mg^{2+} which are activators for isocitric dehydrogenase reactions[6] and the determination of Ca^{2+} and Zn^{2+} activators for alkaline phosphatase[163] have been reported in the last few years.

Determination of inhibitors

There are many substances, called inhibitors, which cause a decrease in the rate of an enzyme-catalysed reaction.[3,6,17] In general, the decrease in the initial rate of an enzymatic reaction is directly proportional to the inhibitor concentration until total inhibition is reached (reaction rate reaches zero). Numerous examples have been reported recently of the determination of most common inorganic anions and cations. Guilbault has compiled a very complete list of the procedures for Ag^+, Al^{3+}, Be^{2+},

Bi^{3+}, Ce^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, In^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, CN^-, $Cr_2O_7^{2-}$, F^- and S^{2-}.[3] Very recently, Townshend and Vaughan have reported the determination of Hg^{2+} and Ag^+ (inhibitors of alcohol dehydrogenase)[164] and Be^{2+} and Zn^{2+} (inhibitors of alkaline phosphatase).[165] With growing concern for the effect of pesticides on the environment and the ecology, there has been considerable research on the application of the selective inhibition of enzyme activity by these substances. Kitz[166] has recently published an extensive review of the inhibition effects on cholinesterase activity, as used for the determination of various organophosphorus compounds. More recently several methods have been reported for a large variety of organophosphorus insecticides, *etc.*[167–174] Methods have been reported for a variety of chlorinated insecticides and herbicides,[171,172,175,176] and carbamate insecticides.[171,172,186–190]

There is a wide variety of factors such as choice of enzyme source and type, substrate, and other reaction conditions, which have considerable effect on the sensitivity and/or selectivity of a reaction for a particular pesticide inhibitor. There have been a large number of studies in this aspect.[180–173,186,189,191,192]

CHEMICAL APPLICATIONS OF RATE METHODS

Comprehensive compilations of the various general chemical applications of kinetic determinations reported before 1969 have been given in two recent books[1,2] and a series of review papers.[11–13,16,183] Druzhinin[184] has reviewed the kinetic-based methods for organic substances, in air-pollution studies. Heil[185] has reviewed kinetic methods applied to water analysis. Thus, this review will list only methods reported during the last two years, except in cases of special importance. These recent publications are listed below in two groups, first the methods for determination of a single species, and second the methods for determination of two or more species by differential reaction rate methods.

Determination of a single component

Inorganic species. The majority of chemical applications of reaction rate methods of analysis have used catalysed reactions and have, in general, employed initial reaction rate procedures. Yatsimirskii has described in detail the techniques and application of catalysed reactions in a recent book.[2]

Klockow, Ludwig and Giraudo[186] have reported the use of a zirconium catalysed reaction between perborate and iodide which can be used for the determination of fluoride. The fluoride acts as an inhibitor in the parts per milliard (ppM) range. Bruton has devised an ion-selective electrode rate method for the determination of both fluoride and chloride.[187] Thompson and Svehla[188] have used the perborate/iodide system for the same type of catalytic determination of iron and molybdenum, and Weisz, Klockow and Ludwig[189] have developed a new electrometric monitoring system for the determination of molybdenum. Cabello-Tomas and West[190] have described a "kineto-chromic" method for trace fluoride determination. Worthington and Pardue have reported a catalytic reaction procedure for the determination of trace ruthenium, using the Ce^{4+} and As^{3+} oxidation-reduction reaction.[191] Janjic, Milovanovic and Celap[192] described a method for the ultramicro determination of manganese by its catalytic action on the oxidation of alizarin by hydrogen peroxide. Analytical applications of the iodine and osmium catalysed reaction between Ce^{4+} and As^{3+} have been discussed by Rodriguez and Pardue.[193] James and Pardue have shown that built-in computer instrumentation is capable of determining levels of 10^{-9}–$10^{-11}M$ osmium, using this reaction system.[103] Kreingol'd and co-workers[194] have described a kinetic method for Cr^{6+} based on the catalysis of oxidation of the herbicide Methurin by potassium bromate. Dolmanova *et al.*[195] also reported a method for Cr^{6+} based on the catalytic oxidation of *o*-dianisidine with hydrogen peroxide. The concentrations of Cu^{2+} solutions have been determined by measuring the effect on the oxidation of furfuraldehyde.[196] Ruthenium has been determined by Ottaway, Fuller and Allan,[197] using the catalysis of the periodate oxidation of the tris[1,10-phenanthroline-iron(II)] complex. Trace determination methods for Ag^+, Hg^{2+} and I^- have been reported by Bognar and Sarosi,[198] based on the catalytic Ag^+–I^- and Hg^{2+}–I^- titrations and the IO_3^-–AsO_3^{3-} Landolt-type indicating system. Lazarev and Lazareva[199,200] have devised two different kinetic methods for V^{5+}. They made use of the catalytic action of V^{5+} on the bromate/5-amino-*N*-phenylanthranilic acid system[199] or the bromate/primary aromatic amine system.[200] Yatsimirskii and Kalinina[201] have also devised a trace vanadium method (0·01–100 ppM) based on the catalytic effect on the iodide oxidation by bromate. Hems, Kirkbright and West[202] have employed the catalytic effect of SO_4^{2-} on the zirconium/Methylthymol Blue reaction, for the determination of sulphate ion. A stopped-flow method for the kinetic determination of Fe^{3+} reacting with thiocyanate ion[23] and Sr^{2+} by a DCTA ligand-exchange reaction have been reported recently.[31]

A method for the determination of trace Cu^{2+} by means of the catalytic effect on the oxidation of amidol by hydrogen peroxide has been reported by Kreingol'd *et al.*[203] Trace methods for the determination of Mn^{2+} by the catalytic effect on the oxidation of Indigo Carmine has been developed by Slychev and Tiginyanu.[204] The Mn^{2+} catalysis of the oxidation of *p*-phenetidine by potassium perchlorate has also been employed in a trace analysis method.[205] A kinetic method for Mn^{2+} has been reported[205] which follows the complexation reaction rate with a sodium carminate–ethylenediamine system, using an integral variant technique. The catalytic effect of iridium on the oxidation of diphenylamines by cerium(IV) has been used in an analytical application by Tikhonova and Yatsimirskii.[207] Yatsimirskii *et al.* have also reported a kinetic method for the determination of iridium, which has been applied to paper chromatographic separation of noble metals.[208] A kinetic method for the determination of cobalt in vitamin B12 uses the catalysis of oxidation of the dye Bordeaux S by hydrogen peroxide.[209] Another catalytic method for Co^{2+} has been reported by Costache and Popa[210] which uses the Bromopyrogallol Red oxidation by peroxide. Filippou, Zyatkovskii and Yatsimirskii have employed the catalysis of the *p*-phenetidine/bromate reaction by Os^{8+} for trace analysis.[211] Segeda[212] has used the Ti^{3+} reaction with hydroxylamine as the basis of a rate method. Bilidiene, Cepelionyte and Jesinskiene[213] have reported a trace Cr^{6+} method based on the catalysis of the Methyl Orange oxidation by hydrogen peroxide. Trace Ag^+ has been determined by means of the catalytic effect on the oxidation of azo dyes by $K_2S_2O_5$.[214] A novel technique for the determination of either Rh^{3+} or Pd^{2+} by catalysis of the reduction of AgBr to Ag in a photographic emulsion by metol–hydroquinone developer has been reported by Pilipenko, Markova and Kaplan.[215]

Several reaction-rate modifications of the classic molybdenum blue method for the determination of inorganic phosphate have been reported.[79,84,98,216,217] These techniques employ either fixed-time or variable-time initial reaction rate measurement.

Similar methods employing the measurement of the initial rates of formation of heteropolymolybdate have been devised by Hargis for the determination of bismuth.[218]

Toropova and co-workers[219] have used an electroanalytical method of measuring the catalytic hydrogen wave of the cobalt–5-sulpho-8-mercaptoquinolinate complex to determine trace amounts of Sb^{3+}. Lukaweiwicz and Fitzgerald[220] have devised a fast photokinetic method for the determination of Fe^{3+}.

Organic species. Gilbert[221] has reported a pulse polarographic method which uses the Co^{2+} catalytic hydrogen wave for determining trace amounts of cystine. Rodziewicz *et al.*[222] have proposed a kinetic method for the determination of various phenolic compounds. A very sensitive method for the estimation of RNA by the Cu^{2+} catalysed orcinol reduction reaction has been reported.[223] Tutt and Schwartz[224] have devised a spectrophotometric assay of Ampicillin (α-aminobenzyl penicillin) involving a maximum rate method. The catalytic polarographic prewave of Ni^{2+} organic diamine systems has been proposed as a means of measuring the pK values of certain sparingly soluble organic amines.[225] A kinetic method for the determination of the stability constants of various metal complexes has been reported by Cohen and Connors.[226] Pillai, Lakshmenon, and Saryanarayana[227] have described a "redoxokinetic" titration method for organic acids. Szepesi and Gorog have reported a method for the determination of organic amines, which follows the rate of the acetylation or formylation reactions.[228]

Simultaneous analysis of mixtures

Inorganic systems. Margerum *et al.*[31] have reported a differential reaction rate method for the analysis of binary and ternary mixtures of lanthanides, transition metals, group II and group III metals, as DCTA complexes reacted with H^+ and/or an exchanging metal ion. Pausch and Margerum[23] have also reported the use of a stopped-flow spectrophotometric method for the simultaneous analysis of binary mixtures of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}, using the exchange reactions of Pb^{2+} with alkaline earth metals complexes. Willis *et al.*[24] have improved this method by employing computer control and data reduction. Rodriguez and Pardue[229] have used the iodide and osmium catalysis of the Ce^{4+}–As^{3+} reaction for the simultaneous determination of I^- and Os^{8+}. Ingle and Crouch have reported a simultaneous differential rate procedure for silicate and phosphate in mixtures.[230]

Organic systems. Lohman and Mulligan have analysed mixtures of ethanolamides by a differential saponification rate method.[231] A kinetic method for the analysis of mixtures of glycols, using the cleavage reaction with lead(IV) has been reported by Benson and Fletcher.[232] Binary ketone mixtures have been determined by Toren and Gnuse[93] by taking advantage of the differences in the reaction rates with hydroxyamine hydrochloride. Greinke and Mark[48] have used the same reagent in the determination of various carbonyl mixtures. Zaia, Peruzzo and Plazzogna have reported a differential reaction rate method for mixtures of various hexa-alkyl-ditin compounds.[233] Shresta and Das have reported a second-order graphical extrapolation method for the simultaneous analysis of various organic amine mixtures.[234]

FUNDAMENTAL KINETIC STUDIES RELATED TO ANALYTICAL PROBLEMS

There have been numerous papers in the recent literature concerned with basic or fundamental kinetic studies on chemical systems which are either directly or indirectly related to analytical methods and procedures. Some of the basic work is intended to develop new methods and reactions for kinetic-based analytical techniques and some is intended to determine the mechanism of reactions involved in the more common equilibrium (or thermodynamic) methods. Once the details of such reaction mechanisms are known, it is possible to systematically improve a method. Recent papers in these two catagories are listed below. It should be pointed out that there is a huge volume of literature devoted to both inorganic and organic chemistry which involves the measurement of kinetic characteristics. It has been pointed out previously that this literature is a wealth of potentially analytically useful systems.[1,7] While this review will not attempt to list the publications in this area of research, the reader should be aware of its existence when faced with devising an analytical procedure for a new problem. There are a number of recent reviews of kinetic studies of the reactions of both organic[235–254] and inorganic species.[255–261]

Perhaps one of the major advances in sensors for rapid and selective *in situ* analysis has been the breakthrough in the theory and design of ion-selective electrodes. These have already been employed in a huge number of equilibrium (potentiometric) analytical methods. Recently Rechnitz and co-workers have also demonstrated that ion-selective electrodes are applicable as sensors in kinetic measurements.[60,61,63,64,262–269] They have studied metal complex reactions,[63,64,262,265,266] instrumentation considerations,[61,267] fast reaction applications[268] and biological systems.[60] Friedman, Palaty and Nakashima[270] have used ion-selective glass electrodes in the study of alkali metal ion-exchange processes. Honaker and Freiser[271] and McClellan and Freiser[272] have shown that solvent extraction methods can be employed, under certain conditions, to study the kinetics of fast chelation reactions. Subbaraman, Cordes and Freiser[273] have also studied the affect of auxiliary complexing agents on the rate of Zn^{2+} and Ni^{2+} extraction with diphenythiocarbazone. McClellan and Menis[19] have studied the kinetics and the mechanism of Fe^{2+} extraction with β-isopropyltropolone. Although there have been no direct applications taking advantage of the differential kinetics of extraction processes reported in the recent literature, it is obvious that there is a potential for future development. Hans has published a theoretical paper on electrolyte extraction kinetics.[275]

As the various organic and inorganic forms of phosphate are now recognized as a very large pollution hazard with respect to the ecological balance in natural water systems, the problem of trace determination of phosphates has received considerable attention in the recent literature. The standard colorimetric and/or spectrophotometric method for inorganic phosphate is the reaction with molybdate to form the 12-molybdophosphoric heteropoly acid species. There have been kinetic mechanism studies of these reactions by Javier, Crouch and Malmstadt.[276] In similar kinetic studies which have analytical significance, Hargis and co-workers have studied the reactions for the formation of silicon and bismuth heteropolymolybdates.[218,277–279] Solkovikov and Prinachek have reported the study of the mechanism and kinetics of the reaction of Al^{3+} with hafnium–molybdenum heteropoly acids.[280] Also in the area of environmental problems, Weber and co-workers have reported on studies of the rates of adsorption of organic pollutants,[284] pesticides,[281] and alkylbenzenesulphonates[282,283] on various activated carbons. These studies have potential for the improvement of activated carbon through a better understanding of the adsorption mechanism, and also for the determination and separation of various pesticides and pollutants.[285]

It is important to point out here that another group[286,287] has reported a kinetic-based pollution treatment system based on the *misinterpretation* of the results of Weber and Morris.[282,283]

In the past few years there have been a number of kinetic analytical methods reported that employ ligand-exchange reactions of metal ion complexes. These initial efforts in this area indicate that these types of metal ion complex reaction have considerable promise for broad analytical application, as discussed in a previous section of this review. Because of this potential certain recent papers describing fundamental kinetic and mechanism studies of metal ion complex systems are listed here. Funashashi and Tanaka[288–290] have studied the ligand-exchange reactions of various Co^{2+}, Cu^{2+} and Ni^{2+} complexes with 4-(2-pyridylazo)resorcinol. Frost and Hart have studied the ligand transfer kinetics of reactions of Eu^{3+}–(2,2,6,6-terpyridine) complexes with Tb^{3+}.[291] The kinetics and mechanism of other ligand transfer reactions have also been reported.[292] Ligand-exchange reactions of cobalt complexes have been reported.[293] Carr and Reilley[294] have reported a study on the kinetics of the ligand-exchange reaction of ethylenediaminetetra-acetate ion with ethylenediamine-tetra-acetatonickel(II). Pausch and Margerum,[31] and Willis *et al.*[25] have studied the ligand-exchange kinetics of strontium complexes of *trans*-DCTA and hydrogen ion, using Pb^{2+} as a scavenger.

Recently there have been several reports on kinetic studies using thermogravimetric methods. Sharp and Wentworth,[295] Carroll and Manche,[296] and Wentworth and Sharp[297] have had an exchange of correspondence on this subject. Taylor and Watson[298] have reported a method of determining relative reaction rates by a differential thermal analysis method. Cerceo[299] has used an evaporation-rate method to determine the degree of "cure" of polymeric materials. Dorko and co-workers have developed a differential scanning calorimetric method for studying the kinetics of solid state reactions.[300] The application of scanning calorimetry to thermal kinetic studies has been reported by Rogers and Smith.[301] Thermogravimetric studies of decomposition reaction rates have been reported by Savin[302] and reviewed by Sestak[303] and by Skvara and Satava.[304]

Hammer and Craig[305] have studied the kinetics of the β-chloroamine reaction and Joris, Aspila and Chakrabarti[306] have reported the results of the decomposition reactions of monoalkyldithiocarbamates. Sand and Huber have developed a differential constant-current potentiometric method for application to kinetic-based analysis.[307] Frankel[308] has devised a nuclear magnetic resonance technique for following the rates of ion-exchange reactions.

Froede and co-workers[309] have reported the development of a rapid-sampling system for use in studying intermediate-speed reactions. A rapid method for the determination of first-order reaction rate constants has been described by Viale[310] and Roy and Al-Jallo[311] have reported a spectrophotometric study of the kinetics of saponification reactions of alkyl ester compounds. Patton and Langer[312] have reported an interesting reaction kinetic method for the detection of void zones in gas chromatographic columns. Rodriguez and Pardue[230] have made an extensive study of the iodine-catalysed reaction between Ce^{4+} and As^{3+} in sulphuric acid. Other studies of the kinetics of catalysed reactions of potential analytical interest have also been reported. The catalytic effect of Cu^{2+} and Fe^{3+} ions on the reaction of Pu^{3+} with chlorine in chloride solutions has been reported by Mazumdar *et al.*[313]

Habig, Pardue and Worthington[314] have found that the catalysis of the reaction between Ce^{4+} and As^{3+} by Os^{7+} is first-order with respect to Os^{7+} over a wide concentration range. With another osmium-catalysed system, Domka and Marciniec[315] have shown that OsO_4 catalyses the decomposition of hydrogen peroxide and the oxidation of Indigo Carmine with peroxide. Yoshiro and co-workers[316] have reported on the Cu^{+}-catalysed oxidation of Mo^{5+} solutions. The activity of Ag^{+} as a catalyst in the oxidation of Tl^{+} by Ce^{4+} has been studied by Zeltmann.[317] Bhat and Khan[318] have studied the catalytic effects of F^{-} and Cl^{-} on the oxidation reactions of various metal ions.

In other kinetic studies of analytical interest, Burkhart and Newton[319] studied the redox kinetics of V^{2+} and Np^{4+} reactions, Flechon and Chavane[320] studied the reduction of silver salts by EDTA, and Matyakha and co-workers[321] have reported kinetic studies of reduction of Ce^{4+} oxalate complexes by hydrogen peroxide. In other redox reaction studies, Krishna and Singh[322] have reported results on the oxidation of I^{-} by ferricyanide in acid media, Davies and co-workers[323] have reported on the Mn^{2+}–H_2O_2 reaction, and Goldberg and Obukhova[324] have studied Mn^{2+} reduction by caproic acid. Everett and Skoog have made a kinetic study of the As^{3+} and Ce^{4+} redox reaction.[325]

Tockstein and Tocksteinova[326] have developed a unique oxidation-reduction titration which they called a *kinetic titration.* They employed the measurement of the rate of change of potential with time, using a zero faradaic current condition as titrant is continuously added. They report that they were able to determine two substances with exactly the same formal potentials provided the reaction rate constants were different by about two orders of magnitude. Sinfelt has reviewed the applied applications of reaction kinetics and catalytic reactions.[327] Samandi and Jaky have studied the mechanism of the oxidation of various organic carboxylic acids with permanganate.[328] Masood, Shastri and Krishna[329] have studied the effects of the nature and concentration of electrolytes on the kinetics of the alkaline fading of phenolphthalein. Smith[330] has recently published a second edition of the book, *Chemical Engineering Kinetics*, which contains extensive information on applied uses of reaction kinetics and other information of potential analytical interest.

Zusammenfassung—Es wird eine Übersicht über Prinzipien und Anwendung katalytischer und kinetischer Analysenmethoden gegeben.

Résumé—On présente une revue des principes et applications des méthodes d'analyse par catalyse et vitesse de réaction.

REFERENCES

1. H. B. Mark Jr., G. A. Rechnitz and R. A. Greinke, *Kinetics in Analytical Chemistry*, Wiley-Interscience, New York 1968.
2. K. B. Yatsimirskii, *Kinetic Methods of Analysis, Pergamon, Oxford*, 1966.
3. G. G. Guilbault, *Enzymatic Methods of Analysis*, Pergamon, Oxford, 1970.
4. H. V. Bergmeyer, Ed., *Methods of Enzymatic Analysis*, 2nd Ed., Verlag Chimie, Meinheim, 1965.
5. R. Ruyssen and E. L. Vandenriesche, Eds. *Enzymes in Clinical Chemistry*, Elsevier, Amsterdam, 1965.
6. W. J. Blaedel and G. P. Hicks, in *Advances in Analytical Chemistry and Instrumentation*, Vol. 3, C. N. Reilley, Ed., p. 105. Wiley-Interscience, New York, 1964.
7. H. B. Mark, Jr., L. J. Papa, and C. N. Reilley, in *Advances in Analytical Chemistry and Instrumentation*, Vol. 2, C. N. Reilley, Ed., p. 255. Wiley-Interscience, New York, 1963.
8. J. Janata, in *Computers in Chemistry and Instrumentation.* Vol. 3, J. S. Mattson, H. C. MacDonald Jr. and H. B. Mark Jr., Eds., in press. Dekker, New York, 1972.

9. H. L. Pardue in *Advances in Analytical Chemistry and Instrumentation*, Vol. 7, C. N. Reilley and F. W. McLafferty, Eds., p. 141. Wiley-Interscience, New York, 1968.
10. S. R. Crouch in *Computers in Chemistry and Instrumentation*, Vol. 3, J. S. Mattson, H. C. MacDonald Jr. and H. B. Mark Jr., Eds., in press. Dekker, New York, 1972.
11. G. A. Rechnitz, *Anal. Chem.*, 1964, **36**, 453R.
12. *Idem, ibid.*, 1966, **38**, 513R.
13. *Idem, ibid.*, 1968, **40**, 455R.
14. G. G. Guilbault, *ibid.*, 1966, **38**, 527R.
15. *Idem, ibid.*, 1966, **40**, 459R.
16. *Idem, ibid.*, 1970, **42**, 334R.
17. *Idem, Crit. Revs. Anal. Chem.*, 1970, **1**, 377.
18. H. U. Bergmeyer, *Z. Anal. Chem.*, 1965, **211**, 77.
19. T. M. Devlin, *Anal. Chem.*, 1959, **31**, 977.
20. M. Roth, *Methods in Biochem. Anal.*, 1969, **17**, 189.
21. T. E. Weichselbaum, W. H. Plumpe Jr., R. E. Adams, J. C. Hagerty and H. B. Mark Jr., *Anal. Chem.*, 1969, **41**, 725.
22. H. V. Malmstadt and S. R. Crouch, *J. Chem. Educ.*, 1966, **43**, 340
23. D. W. Margerum, J. B. Pausch, G. A. Nysseu and G. F. Smith, *Anal. Chem.*, 1969, **41**, 233.
24. B. G. Willis, W. H. Woodruff, J. R. Frysinger, D. W. Margerum and H. L. Pardue, *ibid.*, 1970, **42**, 1350.
25. B. G. Willis, J. A. Bittikofer, H. L. Pardue and D. W. Margerum, *ibid.*, 1970, **42**, 1340.
25a. J. Janata and H. B. Mark Jr., in *Electroanalytical Chemistry*. Vol. 3, ed. A. J. Bard, p. 1. Dekker, New York, 1968.
26. H. B. Mark Jr., *Anal. Chem.*, 1965, **36**, 1668.
27. G. G. Guilbault, M. H. Sadar and K. Peres, *Anal. Biochem.*, 1969, **31**, 91.
28. G. G. Guilbault and S. H. Sadar, *ibid.*, 1971, in press.
29. T. S. Lee and J. M. Kolthoff, *Ann. Acad. N.Y. Sci.*, 1951, **53**, 1093.
30. R. G. Garmon and C. N. Reilley, *Anal. Chem.*, 1962, **34**, 600.
31. J. B. Pausch and D. W. Margerum, *ibid.*, 1969, **41**, 226.
32. J. D. Roberts and C. Regan, *ibid.*, 1952, **24**, 360.
33. R. A. Greinke and H. B. Mark Jr., *ibid.*, 1966, **38**, 340.
34. S. Siggia and J. G. Hanna, *ibid.*, 1961, **33**, 896.
35. C. N. Reilley and L. J. Papa, *ibid.*, 1962, **34**, 801.
36. L. J. Papa, H. B. Mark Jr. and C. N. Reilley, *ibid.*, 1962, **34**, 1513.
37. E. O. Schmalz and G. Geiseler, *Z. Anal. Chem.*, 1962, **188**, 241.
38. *Idem, ibid.*, 1962, **188**, 253.
39. *Idem, ibid.*, 1962, **190**, 222.
40. *Idem, ibid.*, 1962, **190**, 233.
41. J. D. Ingle Jr. and S. R. Crouch, *Anal. Chem.*, 1971, **43**, 697.
42. H. B. Mark, Jr., R. A. Greinke and L. J. Papa, *Proc. Soc. Anal. Chem. Conf., Nottingham, England*, 1965, p. 490.
43. R. A. Greinke, and H. B. Mark, *Anal. Chem.*, 1966, **38**, 340.
44. *Idem., ibid.*, 1966, **38**, 1001.
45. F. Willeboordse and F. E. Crutchfield, *ibid.*, 1964, **36**, 2270.
46. F. Willeboordse and R. L. Meeker, *ibid.*, 1966, **38**, 859.
47. S. Siggia and J. G. Hanna, *ibid.*, 1964, **36**, 228.
48. R. A. Greinke and H. B. Mark Jr., *ibid.*, 1966, **38**, 1001.
49. T. E. Weichselbaum, W. H. Plumpe Jr. and H. B. Mark Jr., *ibid.*, 1969, 41 (No. 3), 108A.
50. P. A. Loach and R. J. Loyd, *ibid.*, 1966, **38**, 1709.
51. H. L. Pardue and P. A. Rodriguez, *ibid.*, 1967, **39**, 901.
52. H. L. Pardue and S. N. Deming, *ibid.*, 1969, **41**, 986.
53. J. D. Ingle Jr. and S. R. Crouch, *ibid.*, 1971, **43**, 1331.
54. M. L. Franklin, G. Horlick and H. V. Malmstadt, *ibid.*, 1969, **41**, 2.
55. R. B. Johnson, *Clin. Chem*, 1969, **15**, 108.
56. A. Vaughan, G. G. Guilbault and D. Hackney, *Anal. Chem.*, 1971, **43**, 721.
57. R. D. Schroeder, in *Computers in Chemistry and Instrumentation*, Vol. 2, J. S. Mattson, H. C. MacDonald Jr., and H. B. Mark Jr., Eds., p. 259. Dekker, New York, 1972.
58. H. V. Malmstadt and H. L. Pardue, *Anal. Chem.*, 1961, **33**, 1040.
59. M. J. D. Brand and G. A. Rechnitz, *ibid.*, 1970, **42**, 1172.
60. B. Fleet and G. A. Rechnitz, *ibid.*, 1970, **42**, 690.
61. G. A. Rechnitz, *ibid.*, 1969, **41**, (12) 109A.
62. G. A. Rechnitz and T. M. Hseu, *ibid.*, 1969, **41**, 111.
63. G. A. Rechnitz and A. F. Lin, *ibid.*, 1968, **40**, 696.

64. K. Srinavsan and G. A. Rechnitz, *ibid.*, 1968, **40**, 1818.
65. H. L. Pardue, *ibid.*, 1963, **35**, 1240.
66. H. B. Mark Jr. and R. A. Greinke, *J. Chem. Educ.*, 1969, **216**, 869.
67. R. A. Greinke and H. B. Mark Jr., *Anal. Chem.*, 1966, **38**, 390.
68. L. P. Papa, J. H. Paterson, H. B. Mark Jr. and C. N. Reilley, *ibid.*, 1963, **35**, 1889.
69. C. N. Reilley, *J. Chem. Educ.*, 1962, **39**, A853.
70. D. E. Johnson and C. G. Enke, *Anal. Chem.*, 1970, **42**, 329.
71. M. Van Swaay, *J. Chem. Educ.*, 1969, **46**, A515.
72. *Idem, ibid.*, 1969, **46**, A565.
73. P. D. Feil, D. G. Kubler and D. J. Wells Jr., *Anal. Chem.*, 1969, **41**, 1908.
74. T. E. Weichselbaum, R. E. Smith and H. B. Mark Jr., *ibid.*, 1969, **41**, 1913
75. E. M. Cordos, S. R. Crouch and H. V. Malmstadt, *ibid.*, 1968, **40**, 1812.
76. G. P. Hicks, A. A. Eggert and E. C. Toren Jr., *ibid.*, 1970, **42**, 729.
77. E. C. Toren Jr., A. A. Eggert, A. E. Sherry and G. P. Hicks, *Clin. Chem.*, 1970, **16**, 215.
78. A. A. Eggert, G. P. Hicks and J. E. Davis, *Anal. Chem.*, 1971, **43**, 736.
79. J. D. Engle Jr. and S. R. Crouch, *ibid.*, 1970, **42**, 1055.
80. H. L. Pardue, C. S. Frings and C. J. Delaney, *ibid.*, 1965, **37**, 1426.
81. H. L. Pardue, M. F. Burke and D. O. Jones, *J. Chem. Educ.*, 1967, **44**, 684.
82. R. H. Stehl, D. W. Margerum and J. J. Latterell, *Anal. Chem.*, 1967, **39**, 1346.
83. G. E. Jamea and H. L. Pardue, *ibid.*, 1968, **40**, 796.
84. S. R. Crouch, *ibid.*, 1969, **41**, 880.
85. H. L. Pardue, R. A. Parker and B. G. Willis, *ibid.*, 1970, **42**, 56.
86. H. L. Pardue, *ibid.*, 1964, **36** 633.
87. *Idem, ibid.*, 1969, **36** 1110.
88. H. L. Pardu and W. E. Dahl, *J. Electroanal. Chem.*, 1964, **8**, 268.
89. H. V. Malmstadt and S. R. Crouch, *J. Chem. Educ.*, 1968, **43**, 340.
90. S. R. Crouch and H. V. Malmstadt, *Anal. Chem.*, 1967., **39**, 1090.
91. D. Pinkel and H. B. Mark Jr., *Talanta*, 1965, **12**, 491.
92. E. C. Toren Jr. and J. E. Davis, *Anal. Lett.*, **1**, 289.
93. E. C. Toren Jr. and M. K. Gnuse, *ibid.*, 1968, 1968, **1**, 295.
94. M. K. Schwartz and O. Bodansky, in *Methods of Biochemical Analysis*, Vol. XI, D. Glick, Ed., p. 211. Wiley-Interscience, New York, 1963.
95. Technicon Instrument Company, *Automation in Analytical Chemistry*, Mediad, White Plains, New York, 1967.
96. H. V. Malmstadt and G. P. Hicks, *Anal. Chem.*, 1960, **32**, 445.
97. H. V. Malmstadt and H. L. Pardu, *ibid.*, 1962, **34**, 299.
98. A. C. Javier, S. R. Crouch and H. V. Malmstadt, *ibid.*, 1969, **41**, 239.
99. S. N. Deming and H. L. Pardue, *ibid.*, 1971, **43**, 192.
100. K. A. Mueller and M. F. Burke, *ibid.*, 1971, **43**, 641.
101. C. F. Fasce Jr. and R. Rej, *Clin. Chem.*, 1970, **16**, 972.
102. K. G. Sorokin, M. I. Gromov and A. M. Chernyskii, *Vestn. Akad. Nauk Kaz. SSR*, 1970, **26**, 21.
103. G. E. James and H. L. Pardue, *Anal. Chem.*, 1969, **41**, 1618.
104. J. Janata and H. B. Mark Jr., in *Electroanalytical Chemistry*, Vol. 3, A. J. Bard, Ed., p. 1. Dekker, New York, 1968.
105. S. P. Perone, D. O. Jones and W. F. Gutknecht, *Anal. Chem.*, 1969, **41**, 1154.
106. S. P. Perone, in *Computers in Chemistry and Instrumentation*, Vol. 2, J. S. Mattson, H. C. MacDonald Jr., and H. B. Mark Jr., Eds., p. 423. Dekker, New York, 1972.
107. W. C. Purdy, *Electroanalytical Methods in Biochemistry* McGraw-Hill, New York, 1965.
108. S. Udenfriend, *Fluorescence Assay in Biology and Medicine*, Academic Press, New York, 1962.
109. R. Ruyssen and E. L. Vandenriesche, Eds., *Enzymes in Clinical Chemistry*, Elsevier, Amsterdam, 1965.
110. G. G. Guilbault, in *Fluorescence, Theory, Instrumentation, and Practice*, G. G. Guilbault, Ed., p. 297ff. Dekker, New York, 1967.
111. R. E. Phillips and F. R. Elevitch, in *Progress in Clinical Pathology*, M. Steffani, Ed., p. 62ff. Greene and Stratton, New York, 1966.
112. S. Danev, *Suurem. Med.*, 1970, **21**, 33.
113. P. Zuman, *Methods Enzymol.*, 1969, **16**, 121.
114. G. G. Guilbault, M. H. Sadar, R. Glazer and C. Skoa, *Anal. Lett.*, 1968, **1**, 365.
115. G. G. Guilbault and R. Zimmerman, *ibid.*, 1970, **3**, 133.
116. G. G. Guilbault and A. Heyn, *ibid.*, 1968, **1**, 163.
117. G. G. Guilbault, D. N. Kramer and E. Hackley, *Anal. Biochem.*, 1967, **18** 241.
118. G. G. Guilbault and M. H. Sadar, *Anal. Lett.*, 1968, **1**, 551.
119. G. G. Guilbault and J. Hieserman, *Anal. Chem.*, 1968, **41**, 2006.
120. G. G. Guilbault, M. H. Sadar, R. Glazer and J. Haynes, *Anal. Lett.*, 1968, **1**, 333.

121. G. G. Guilbault and A. Vaughan, *ibid.*, 1970, **3**, 1.
122. R. B. Johnson, *Clin. Chem.*, 1969, **15**, 108.
123. A. Vaughan, G. G. Guilbault and D. Hackney, *Anal. Chem.*, 1971, **43**, 721.
124. G. G. Guilbault and H. Hieserman, *Anal. Biochem.*, 1968, **26**, 1.
125. G. G. Guilbault, P. Brignac and M. Zimmer, *Anal. Chem.*, 1968, **40**, 190.
126. *Idem, ibid.*, 1968, **40**, 1256.
127. G. G. Guilbault and D. N. Kramer, *ibid.*, 1964, **36**, 2497.
128. *Idem, ibid.*, 1965, **37**, 1219.
129. G. E. James and H. L. Pardue, *ibid.*, 1968, **40**, 796.
130. G. G. Guilbault, D. N. Kramer and P. L. Cannon, *ibid.*, 1962, **34**, 842.
131. G. G. Guilbault, B. Tyson, D. N. Kramer and P. L. Cannon, *ibid.*, 1968, **35**, 582.
132. G. G. Guilbault, D. N. Kramer and P. L. Cannon, *ibid.*, 1964, **36**, 606.
133. G. G. Guilbault, *Anal. Biochem.*, 1966, **41**, 61.
134. H. V. Malmstadt and H. L. Pardue, *Clin. Chem.*, 1962, **8**, 606.
135. H. L. Pardue, R. Simon and H. V. Malmstadt, *Anal. Chem.* 1964, **36**, 735.
136. H. L. Pardue and R. Simon, *Anal. Biochem.*, 1964, **9**, 204.
137. W. J. Blaedel and C. Olsen, *Anal. Chem.*, 1964, **36**, 343.
138. H. L. Pardue and C. Frings *J. Electronal. Chem.*, 1964, **7**, 398.
139. W. C. Purdy, *Anal. Chem.*, 1964, **36**, (No. 4), 29A.
140. S. A. Katz, *ibid.*, 1964, **36**, 2500.
141. G. G. Huilbault, R. K. Smith and J. G. Montalvo Jr., *ibid.*, 1969, **41**, 600.
142. U. Fischerova-Bergerova, *Pracouni Lekavstvi*, 1964, **16**, 111, 8.
143. T. H. Ridgway and H. B. Mark Jr., *Anal. Biochem.*, 1965, **12**, 357.
144. M. N. Gadaleta, E. Lofrumento, C. Landriscina and A. Alifano, *Bull. Soc. Ital. Biol. Sper.*, 1963, **39**, 1866.
145. H. Jacob, *Z. Chem.*, 1964, **4**, 189.
146. C. C. Curtin, *Anal. Biochem.*, 1964, 8, 184.
147. H. Lipner, L. Witherspoon and A. Wahlborg, *Anal. Chem.*, 1965, **37**, 347.
148. H. V. Malmstadt and E. H. Piepmeier, *ibid.*, 1965, **37**, 34.
149. H. V. Bergmeyer, Ed., *Methods in Enzymatic Analysis*, 2nd Ed., Verlag Chemie, Mernheim, 1965.
150. G. G. Guilbault, S. H. Sadar and R. McQueen, *Anal. Chem. Acta*, 1969, **45**, 1.
151. G. Faway and K. Dahl, *Lebanese Med. J.*, 1963, **16**, 169.
152. A. Mondzac, G. Ehrlich and J. Seegmiller, *J. Lab. Clin. Med.*, 1965, **66**, 526.
153. K. L. Reichelt, E. Kjamme and B. Tviet, *Scand. J. Clin. Lab. Invest.*, 1964, **16**, 433.
154. E. Kirsten, C. Gerez and R. Kirsten, *Biochem. Z.*, 1963, **337**, 312.
155. F. Roch-Ramel, *Anal. Biochem.*, 1969, **21**, 372.
156. M. Rubin and L. Knott, *Clin. Chem. Acta*, 1969, **18**, 409.
157. D. W. Schultz, J. V. Passonneau and O. H. Lowry, *Anal. Biochem.*, 1967, **19**, 300.
158. E. Faway, F. Roth and G. Faway, *Biochem. Z.* 1966, **344**, 212.
159. I. Chibata and T. Tosa, *Tompakushitsu Kakusan Koso*, 1966, **11**, 23.
160. G. P. Hicks and S. J. Updike, *Anal. Chem.*, 1966, **38**, 726.
161. S. J. Updike and G. P. Hicks, *Science*, 1967, **158**, 270.
162. O. H. Lowry, V. Passonneau, D. Schulz and M. K. Rock, *J. Biol. Chem.*, 1961, **236**, 2746.
163. A. Townhend and A. Vaughan, *Talanta*, 1970, **17**, 289.
164. *Idem, ibid.*, 1970, **17**, 299.
165. *Idem, ibid.*, 1969, **16**, 929.
166. R. J. Kitz, *Acta Anaesthes. Scand.*, 1964, **8**, 197.
167. J. Matousek, J. Fischer and J. Cerman, *Chem. Zvesti*, 1968, **22**, 184.
168. S. Saliman, *Ain Shams Sci. Bull.* 1966, **9**, 127.
169. K. Goszezyhska and B. Stycyznska, *Kocz. Panstiu Zukl. Hig.*, 1966, **9**, 127.
169. K. Goszezyhska and B. Stycyznska, *Kocz. Panstiu Zukl. Hig.*, 1968, **19**, 491.
170. G. G. Guilbault, M. H. Sadar and S. Kuan, *Anal. Chim. Acta*, 1972, in press.
171. *Idem, ibid.*, 1972, in press.
172. G. G. Guilbault and M. H. Sadar, *J. Agr. Food. Chem.*, 1971, **19**, 357.
173. G. G. Guilbault, S. Kuan and M. H. Sadar, *ibid.*, 1971, **19**, 415.
174. G. G. Guilbault, M. H. Sadar and M. Zimmer, *Anal. Chim. Acta*, 1969, **44**, 361.
175. H. Keller, *Naturwissenschaften*, 1965, **39**, 109.
176. G. G. Guilbault and M. H. Sadar, *Anal. Chem.*, 1969, **41**, 366.
177. M. B. Abou-Donia and D. B. Menzel, *Comp. Biochem. Physiol.*, 1967, **21**, 99.
178. F. Winteringham and K. S. Fowler, *Biochem. J.*, 1966, **99**, 6P.
179. S. Zhuravskaya and T. Bobyreva, *Uzb. Biol. Zh.*, 1968, **12**, 55.
180. G. Voss, *Bull. Environ. Contam. Toxicol.*, 1968, **3**, 339.
181. J. Cohan, R. Dosterbann and F. Berends, *Methods Enzymol.*, 1967, **11**, 686.

182. J. Delga and P. Foulhoux, *Prod. Probl. Pharm.*, 1969, **24**, 184.
183. R. Bontchev, *Talanta*, 1970, **17**, 499.
184. A. A. Druzhinin, *Zh. Uses Khim. Obstichest*, 1970, **15**, 529.
185. G. Heil, *Haus Tech., Essen., Vortragsveroeff*, 1970, **231**, 29.
186. D. Klockow, H. Ludwig and M. A. Giraudo, *Anal. Chem.*, 1970, **42**, 1682.
187. L. G. Bruton, *ibid.*, 1971, **43**, 519.
188. H. I. Thompson and G. Svehla, *Z. Anal. Chem.*, 1969, **247**, 244.
189. H. Weisz, D. Klockow and H. Ludwig, *Talanta*, 1969, **16**, 921.
190. M. L. Cabello-Tomas and T. S. West, *ibid.*, 1969, **16**, 781.
191. J. B. Worthington and H. L. Pardue, *Anal. Chem.*, 1970, **42**, 1157.
192. T. J. Janjic, G. A. Milovanovic and M. B. Celap, *ibid.*, 1970, **42**, 27.
193. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
194. S. Kreingol'd, E. Bozhevol'nov, G. Supin, V. Antonov and A. Panteleimonova, *Zh. Analit. Khim.*, 1969, **24**, 853.
195. I. Dolmanova, G. Zolotova, L. Tarawova and V. Peshkova, *ibid.*, 1969, **24**, 1035.
196. E. Casassas and H. Torres, *Inform. Quim. Anal.*, 1969, **23**, 61.
197. J. Ottaway, C. Fuller, and J. Allan, *Analyst*, 1969, **94**, 1522.
198. J. Bognar and S. Sarosi, *Urikrokhim. Acta*, 1969, 463.
199. A. Lazarev and V. Lazareva, *Zh. Analit. Khim.*, 1969, **24**, 395.
200. *Idem*, *Opred. Midroprimesei*, 1968, **1**, 95.
201. K. B. Yatsimirskii and V. Kalinina, *Zh. Analit. Khim.*, 1969, **24**, 390.
202. R. Hems, G. Kirkbright and T. S. West, *Talanta*, 1969, **16**, 789.
203. S. U. Kreingol'd, E. A. Boxhevol'nov, V. N. Antonova, A. H. Pauteleimonva and L. J. Sosendova, *Otbrytiya, Izobret. Prom. Obraztsy, Tovarnye Znale*, 1970, **47**, 95.
204. Ya. A. Sychev and Ya. D. Tiginyanu, *Zh. Analit. Khim.*, 1969, **24**, 1842.
205. I. F. Dolmantova, V. P. Poddubiendo and V. M. Peshkova, *ibid.*, 1970, **25**, 2146.
206. P. Bartkus, V. Kalesnikaite, and E. Jasinskiene, *Liet TSR Ankst Mokyklu Moksla Darb. Chem. Technol.*, 1969, **10**, 15.
207. L. P. Tikhonova and K. B. Yatsimirski, *Zh. Analit. Khim.*, 1970, **25**, 1766.
208. K. B. Yatsimirskii, L. P. Tikhonova, G. M. Varshal and V. A. Sychkova, *Proc. Anal. Chem. Conf.* 3rd, 1970, **1**, 191.
209. D. Costache and G. Popa, *Rev. Roum. Chim.*, 1970, **15**, 1061.
210. *Idem*, *ibid.*, 1970, **15**, 1349.
211. A. P. Filippov, V. M. Zyatkovskii and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1970, **25**, 1769.
212. A. S. Segeda, *Ukr. Khim. Zh.*, 1970, **36**, 440.
213. E. Bilidiene, J. Cepelionyte and E. Jesinskiene, *Liet TSR Audst, Mokyklu Mokslo Darb, Chem. Chem. Technol.*, 1969, **10**, 55.
214. E. Jasinskiene and N. Roseviante, *Zh. Analit. Khim.*, 1970, **25**, 458.
215. A. T. Pilipenko, L. V. Markova and M. C. Kaplan, *ibid.*, 1970, **25**, 2414.
216. S. Roselowski, *Chem. Analit. (Warsaw)*, **15**, 157.
217. E. E. Kriss, V. K. Rudenko and K. B. Yatsimirskii, *Zh. Analit. Khim.*, 1970, **25**, 1603.
218. L. G. Hargis, *Anal. Chem.*, 1969, **41**, 597.
219. V. Toropova, L. Anisimova, L. Paolichenko and Y. Bankovskii, *Zh. Analit. Khim.*, 1969, **24**, 1031.
220. R. Lukaweiwicz and J. Fitzgerald, *Anal. Lett.*, 1969, **2**, 159.
221. D. D. Gilbert, *Anal. Chim.*, 1969, **41**, 1567.
222. W. Rodziewicz, I. Kwiatkowski, and E. Kwiatkowski, *Chem. Analit.* (*Warsaw*), 1969, **14**, 55.
223. R. I.-San Lin and O. Schjeide, *Anal. Biochem.*, 1969, **27**, 473.
224. D. E. Tutt and M. A. Schwartz, *Anal. Chem.*, 1971, **43**, 338.
225. J. Čaja and H. B. Mark Jr., *ibid.*, 1971, **43**, 964.
226. J. L. Cohen and K. A. Conners, *Am. J. Pharm. Educ.*, 1970, **34**, 197.
227. K. K. J. Pillai, A. S. Lakshmanan and C. V. Suryonarayana, *Electrochim. Acta*, 1970, **15**, 795.
228. G. Szepesi and G. Gorog, *Proc. Anal. Chem. Conf. 3rd*, 1970, **3**, 145.
229. P. A. Rodriguez and H. L. Pardue, *Anal. Chem.*, 1969, **41**, 1369.
230. J. D. Ingle Jr. and S. R. Crouch, *ibid.*, 1971, **43**, 7.
231. F. Lohman and T. Mulligan, *ibid.*, 1969, **41**, 243 .
232. D. Benson and N. Flecher, *Talanta*, 1966, **13**, 1207.
233. P. Zaia, V. Peruzzo and G. Plozzogna, *Anal. Chim. Acta*, 1970, **51**, 317.
234. I. L. Shreste and M. N. Das, *ibid.*, 1970, **50**, 135.
235. Y. Inel, *J. Phys. Chem.*, 1970, **74**, 2581.
236. M. Caplow, *NASA Spec. Publ.* 1968 (publ. 1969), NASA SA 188.
237. I. I. Moiseev, *Kinet. Katal.*, 1970, **11**, 342.
238. T. Ishir, *Kagaka Kogaka*, 1970, **34**, 477.

239. P. C. Moerk, *Kjemi*, 1970, **30**, 9.
240. K. J. Ivin, *Ann. Rept. Progr. Chem., Sect. A*, 1969, **66**, 121.
241. D. A. Leathard and J. H. Purnell, *Ann. Rev. Phys. Chem.*, 1970, **21**, 197.
242. R. Huisgen, *Angew. Chem. Intern. Ed.*, 1970, **9**, 751.
243. J. Hine, *Physical Organic Chemistry*, Holt, New York, 1959.
244. P. D. Bartlett, G. N. Fickes, F. C. Haupt and R. Helgeson, *Accounts Chem. Res.*, 1970, **3**, 117.
245. L. Dorfman, *ibid.*, 1970, **3**, 224.
246. D. S. Tarbell, *ibid.*, 1969, **2**, 296.
247. E. J. Hart, *ibid.*, 1969, **2**, 161.
248. K. U. Ingold, *ibid.*, 1969, **1**, 1.
249. M. Hanack, *ibid.*, 1970, **3**, 209.
250. J. L. Dye, *ibid.*, 1968, **1**, 306.
251. E. J. Kaiser, *ibid.*, 1970, **3**, 145.
252. E. G. Cordes and R. B. Dunlap, *ibid.*, 1969, **2**, 329.
253. G. Modena, *ibid.*, 1971, **4**, 73.
254. K. Yates, *ibid.*, 1971, **4**, 136.
255. D. M. Chizhikov, *Mekh. Kmet. Vosstanov. Metal. Mater. Simp.*, 1968, 15.
256. H. Taube, *Advan. Chem. Ser.*, 1965, **14**, 107.
257. H. Taube and E. S. Gould, *Accounts Chem. Res.*, 1969, **2**, 321.
258. J. Halpern, *ibid.*, 1970, **3**, 386.
259. G. J. Hoytink, *ibid.*, 1969, **2**, 114.
260. J. H. Espenson, *ibid.*, 1970, **3**, 347.
261. R. G. Wilkins, *ibid.*, 1970, **3**, 408.
262. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1968, **40**, 1955.
263. G. A. Rechnitz, *Accounts Chem. Res.*, 1970, **3**, 69.
264. M. J. P. Brand and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1968.
265. T. Hseu and G. A. Rechnitz, *ibid.*, 1968, **40**, 1054.
266. *Idem*, *Anal. Lett.*, 1968, **1**, 629.
267. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1788.
268. *Idem*, *ibid.*, 1969, **41**, 1185.
269. *Idem*, *ibid.*, 1970, **42**, 616.
270. S. Friedman, V. Palaty and M. Nakashima, *Anal. Biochem.*, 1969, **29**, 107.
271. C. B. Honaker and H. Freiser, *J. Phys. Chem.*, 1962, **66**, 127.
272. B. E. McClellan and H. Freiser, *Anal. Chem.*, 1964, **36**, 2262.
273. P. R. Subbaraman, M. Cordes and H. Freiser, *ibid.*, 1969, **41**, 1878.
274. B. E. McClellan and O. Menis, *ibid.*, 1971, **43**, 436.
275. T. Hark, *Union Burma J. Sci. Tech.*, 1968, **1**, 381.
276. A. Javier, S. R. Crouch and A. V. Malmstadt, *Anal. Chem.*, 1969, **41**, 1922.
277. H. D. Goldman and L. G. Hargis, *ibid.*, 1969, **41**, 490.
278. L. G. Hargis, *ibid.*, 1970, **42**, 1494.
279. *Idem*, *ibid.*, 1970, **42**, 1497.
280. E. N. Sokovikov and O. K. Prinachek, *Vestn. Mosk. Univ., Khim.*, 1970, **11**, 367.
281. W. J. Weber Jr. and J. P. Gould in *Organic Pesticides in the Environment, Adv. Chem. Ser.*, 1966, **60**, 280.
282. W. J. Weber Jr. and J. C. Morris, *J. Sanit. Eng. Div.*, 1963, **89**, 31.
283. *Idem*, *ibid.*, 1964, **90**, 79.
284. V. L. Snoeynk and W. J. Weber Jr., in *Adsorption from Aqueous Solution, Adv. Chem. Ser.*, 1968, **79**, 112.
285. J. S. Mattson and H. B. Mark Jr., *Activated Carbon; Surface Chemistry and Adsorption from Solution*, Dekker, New York, 1971.
286. M. W. Zuckerman, *Ph.D. Thesis*, New York University, 1968.
287. M. W. Zuckerman and A. H. Molaf, *J. Water Pollut. Cont. Fed.*, 1970, **42**, 437.
288. S. Funahashi and M. Tanaka, *Bull. Chem. Soc. Japan*, 1970, **43**, 763.
289. *Idem*, *ibid.*, 1970, **43**, 769.
290. *Idem*, *Inorg. Chem.*, 1969, **8**, 2159.
291. G. H. Frost and F. A. Hart, *J. Chem. Soc. D*, 1970, 836.
292. I. I. Kalinchenko and E. N. Yurchenko, *Spektrosk. Fr. Sib Soveshch, 4th*, 1965, (Publ. 1969), 182.
293. M. J. Hynes, G. D. Dewit and D. A. Sweigart, *Inorg. Chem.*, 1971, **10**, 196.
294. J. D. Carr and C. N. Reilley, *Anal. Chem.*, 1970, **42**, 51.
295. J. H. Sharp and S. A. Wentworth, *ibid.*, 1969, **41**, 2060.
296. B. Carroll and P. Manche, *ibid.*, 1970, **42**, 1296.
297. S. A. Wentworth and J. H. Sharp, *ibid.*, 1970, **92**, 1297.

298. L. J. Taylor and S. W. Watson, *ibid.*, 1970, **42**, 297.
299. E. Cerceo, *ibid.*, 1969, **41**, 191.
300. E. A. Dorko, A. S. Hughes and C. R. Downs, *ibid.*, 1970, **42**, 253.
301. R. N. Rogers and L. C. Smith, *Thermochimica Acta*, 1970, **1**, 1.
302. V. O. Savin, *Zh. Fiz. Khim.*, 1970, **44**, 1046.
303. J. Sestek, *Chem. Listy*, 1970, **64**, 695.
304. F. Skvara and V. Safava, *J. Therm. Anal.*, 1970, **2**, 325.
305. C. F. Hammer and J. A. Graig, *Anal. Chem.*, 1970, **42**, 1588.
306. S. J. Joris, K. L. Aspila and C. L. Chakrabarti, *ibid.*, 1970, **42**, 647.
307. J. R. Sand and C. O. Huber, *ibid.*, 1970, **42**, 238.
308. J. S. Frankel, *ibid.*, 1970, **42**, 1638.
309. H. C. Froede, J. Cowan, T. W. Reid and I. B. Wilson, *ibid.*, 1970, **42**, 1209.
310. R. O. Viale, *ibid.*, 1970, **42**, 1834.
311. R. Roy and H. Al-Jallo, *ibid.*, 1969, **41**, 1725.
312. J. E. Patton and S. H. Langer, *ibid.*, 1970, **42**, 1449.
313. A. Mazumdar, R. Gupta and P. Natarajun, *U.S. At. Energy Comm.*, *Rept.* AETT 275, 1967.
314. R. Habig, H. L. Pardue and J. Worthington, *Anal. Chem.*, 1967, **39**, 600.
315. F. Domka and B. Marciniec, *Chem. Analit.* (*Warsaw*), 1969, **14**, 145.
316. Y. Yoshiro, T. Takeuchi, A. Kinoshita and S. Uchida, *Bull. Chem. Soc. Japan*, 1968, **41**, 765.
317. E. Zeltman, *Diss. Abst. B*, 1967, **28**, 1815.
318. T. Bhat and I. Khan, *J. Less-Common Metals*, 1968, **14**, 240.
319. M. Burkhart and T. Newton, *J. Phys. Chem.*, 1969, **44**, 1741.
320. J. Flechon and F. Chavane, *Bull. Soc. Chim. France*, 1968, 3143.
321. V. Matyakha, V. Milov, N. Kroty and P. Pernimov, *Zh. Neorgan. Khim.*, 1967, **12**, 3331.
322. B. Krisha and H. Singh, *Chim. Anal.* (*Paris*), 1967, **49**, 330.
323. G. Davis, L. Krischenbaum and K. Kristin, *Inorg. Chem.*, 1968, **7**, 146.
324. V. M. Goldberg and L. K. Obukhova, *Vestn. Akad. Nauk USSR*, 1967, **43**, 88.
325. K. G. Everett and D. A. Skeog, *Anal. Chem.*, 1971, **43**, 1541.
326. A. Tockstein and D. Tocksteinova, *Collection Czech. Chem. Commun.*, 1969, **34**, 1625.
327. J. H. Sinfelt, *Ind. Eng. Chem.*, 1970, **62**, 22.
328. L. Samandi and M. Jaky, *Tetrahedron Lett.*, 1970, **40**, 3489.
329. A. Masood, N. K. Shastri, and K. Krishna, *Chim. Anal. Paris*, 1970, **52**, 1289.
330. J. M. Smith, *Chemical Engineering Kinetics*, 2nd Ed., McGraw-Hill, New York, 1970.

Talanta, 1972, Vol. 19, pp. 747 to 760. Pergamon Press. Printed in Northern Ireland

DEVELOPMENT AND PUBLICATION OF NEW TITRIMETRIC METHODS

A. BERKA and J. ŠEVČÍK
Department of Analytical Chemistry, Charles University,
Prague 2, Albertov 2030, Czechoslovakia

ROBERT A. CHALMERS
Chemistry Department, University of Aberdeen, Old Aberdeen,
Scotland

(*Received* 30 *April* 1970. *Revised* 10 *August* 1971. *Accepted* 20 *November* 1971)

Summary—Requirements are laid down for the development of titrimetric methods and for writing up the work for publication. The general principles of various types of titration reaction are discussed, and special attention is paid to the parameters which influence chemical reactions.

ALTHOUGH about 200 years have elapsed since the publication of the first papers dealing with titrimetric analysis,[1] the technique is still as widely used as ever, especially since the development of physicochemical methods of measurement, which permit not only objective detection of the end-point of a titration but also monitoring of the course of the reaction and hence a better understanding of its chemistry. Better understanding in turn leads to improvements in speed, precision, accuracy, sensitivity and/or selectivity of the procedures. In spite of all this, however, many methods are published which leave much to be desired both in their usefulness and in validation of the conditions used. It may be argued that that is the fault of the editors and referees concerned, but it is not really part of their duties to give private tuition in research methods. This paper has therefore been added to those already published on how to develop and write up methods,[2,3] with the intention of fulfilling the need for such instruction.

GENERAL REQUIREMENTS OF A TITRIMETRIC METHOD

In general, as with other analytical methods, titrimetric procedures should be accurate and precise, simple to use, work under a wide range of conditions, fulfil a definite need and have practical applications (otherwise they are merely academic exercises and of little value) and should be rapid (if they are slow they offer no advantage over gravimetric methods). Some of these criteria are worth further comment. By "accurate and precise" we mean that the results should be correct and reproducible within the limits set by the random errors in measurement, and in the research work on a new method it is imperative that the errors be kept as small as possible. If it is known that a method is capable of giving results correct to within 1 part per thousand (1 ppt) then if a larger error is acceptable for some particular application, the method can be used with confidence even if less care is taken. On the other hand, if the best that can be done with a method gives an error of 1%, application of that method is limited to those situations in which a larger error than this can be tolerated. All too often there seems to be a failure to realise that in titrimetry the need to standardize the titrant introduces an additional source of error, since any mistake made in determining the titre will cause a bias in all the results obtained with the titrant. Consider, for example, the standardization of ceric sulphate with arsenious oxide, with osmium tetroxide as catalyst and ferroin as indicator. To give a reasonable titration volume of $0.1M$ ceric sulphate (*i.e.*, about 30 ml, which can be measured with a reading error of about 0.03 ml or less if care is taken), a weight of about 150 mg of arsenious oxide is required. Suppose this is weighed on a normal fourth-place balance with a standard deviation of 0.05 mg at the weight loading used, and that the balance weights have not been calibrated. The random error in weighing by difference will be about 0.15 mg (95% confidence limits) and in addition there may be a biased error from the unknown errors in the weights. The manufacturer's tolerance on weights up to 500 mg is 0·05 mg, and since there must be an exchange of at least two fractional weights it would be possible for this bias to amount to at least 0·1 mg. If this reinforces the random error, we have already an error of nearly 2 ppt in the weight of primary standard taken, plus an expected reading error of 1 ppt. In addition there is the end-point error arising from the fact that we do not know how much of the last increment added was actually required to reach the end-point and how much was excess. "Splitting" drops is tedious, and this error can be minimized by assuming that the end-point was reached on addition of half the last drop. The error is then only half the drop-size. If a varying amount of indicator is added to replicate samples, there will be a variation in the amount of titrant needed to oxidize the indicator, and if the indicator is too concentrated or too large an amount is added (or both!) another biased error can occur. Obviously care and thought are needed to measure the titre to within 1 ppt, and if the standardization is not done accurately, the results of use of the titrant will not be as meaningful as they should be. How often we see in a paper the statement that a solution was standardized by some method or other, usually described only by a reference, and no information is given as to the precision of the results obtained. Similar remarks apply to calibration of apparatus, for which the results are scarcely ever given.

By "simple to use" and "work under a wide range of conditions" we mean that there should be as few procedural steps as possible, since each can lead to a mistake being made, and that tolerances on such factors as pH range, ionic strength, amounts of particular compounds permitted to be present, should be as wide as possible, so that undue care need not be taken over adjustment of conditions. A procedure that requires very close control of pH is not nearly as satisfactory to use as one that operates over a pH range of several units.

By "rapid" we mean that reaction should proceed more rapidly than titrant can be added to the system, or at least very nearly so. A procedure in which a wait of several minutes is necessary between additions of titrant is going to be a very irksome one to use, and not at all suitable for routine analysis. Many potentiometric systems suffer from this drawback, when the electrode system used takes some time to reach a stable potential as the titration proceeds. Sometimes, of course, a slow reaction can be combined with a back-titration that is rapid, by adding an excess of reactant, leaving it for a sufficient time, and then titrating the excess. Again, an interfering reaction may be made to occur so slowly that it does not affect the main reaction, or the kinetics may already be sufficiently different for no interference to occur.

By "fulfilling a need and having practical application" we mean that a reaction that is suitable only for analysis of a pure solution of the substance to be determined is of such limited usefulness as to be practically worthless unless it is so very much better than any other available method that it is necessarily the method of choice for standardizing solutions of that substance. This was stated very clearly over 30 years ago by Lundell in his paper "Analysis of Things as They Are",[4] a paper that should be compulsory reading for all analytical chemists. The literature is full of "new and improved" methods that are in fact poorer in performance than the ones they seek to replace, and that are often based on standardizations performed by means of methods that they criticize and claim to supplant. Many methods have been published for the titrimetric determination of iron, but very few of them are better than the earliest methods of all—oxidation of iron(II) with dichromate[5] or permanganate.[6]

Unless the method being developed promises to fulfill these criteria, it seems scarcely worth while pursuing it. If it *does* show promise, however, there must be a proper investigation of the conditions under which it should be used, and a proper assessment of its scope of application and of its reliability. The remainder of this paper will deal with these aspects. Each type of reaction will be dealt with separately, as will standardization and end-point detection.

BASIC CONDITIONS OF TITRIMETRIC DETERMINATIONS

Only those reactions which proceed in stoichiometric ratio in a chosen solvent, without side-reactions and consecutive reactions, can serve as a basis for titrimetric determinations. The end-point of the reaction must be detectable by chemical or physical means.

Special demands are made of the substance used as titrant. It must be of well defined composition, easily soluble in the chosen solvent so that solutions covering a wide range of concentration can be prepared, and its solutions should either be stable or easily standardized. Some titrants which are unstable because of reactions with the solvent or the atmosphere, or because of volatility or light-sensitivity, can still be used if the active species is generated *in situ* electrolytically. It is desirable that the substance should be readily available.

Although a detailed study of the kinetics is not essential for development of a titrimetric method, it stands to reason that a method that is kinetically slow is not a very useful one, especially for routine work. However, slow reactions may be used in indirect methods if the back-titration reaction is fast. On the other hand, a competing reaction may be suppressed by proper adjustment of the conditions if its rate of reaction is much slower than that of the main reaction. Similarly it is not essential that the mechanism of the reaction be known, though again, knowledge of it may be useful in certain circumstances. The stoichiometry can be expressed in terms of equivalents or of the ratio of molar concentrations, which should be a ratio between small integers. It is worth stating at this point that in titrimetry it is essential to retain both the mole-concept and the concept of normality. Each has its own special field of application, together with an enormous overlap of applicability, where either can be used. For example, in dealing with polymers and many biochemical systems, it is not known (or cannot be known) what the molecular weight is, although it is perfectly easy to determine the number of equivalents of some reactive group in a given weight of sample. In contrast, normality is meaningless in complexation reactions. For the rest, the objection to the use of equivalents, *viz.* that a different equivalent weight must be used for different reactions of the same substance, is just as much an objection to the use of moles, because the equation must be written down in both cases, and the only real difference is in the point at which the stoichiometric coefficients are introduced into the calculation. If the equivalent is defined as that weight of material which will react with one mole of hydrogen ions or of electrons or with one equivalent of any other substance, both conventions are referred unambiguously to the mole concept, and there should be no difficulty in understanding and applying both.

Assumptions about stoichiometry are best verified by using equimolar solutions of the titrant and titrand and seeing whether the volumes needed to complete the reaction are in some simple whole-number ratio. If they are not, then either the reaction is non-quantitative for kinetic or thermodynamic reasons, or the main reaction is accompanied by side-reactions or consecutive reactions. Because these latter reactions can proceed at a considerably lower velocity than the main reaction, it is convenient to add an excess of titrant and to determine the amount unreacted after a sufficient time, to verify that there is no consecutive reaction. The stoichiometry can also be checked by quantitative determination of the reaction products. In direct titrations (see below), a titration error can be falsely attributed to non-quantitative reaction if the stoichiometry is not checked. It is often difficult, however, to decide whether non-quantitative results are due to the kinetics or the thermodynamics.[7]

Precipitation reactions

The main criterion is the value of the solubility product for the substance being precipitated. If C_M is the initial concentration of the metal to be precipitated by the titrant, then for 1 ppt error (which we will take as the working error to be aimed at) the final concentration must be $10^{-3}\,C_M$, and for a precipitate ML the apparent solubility product must be $10^{-6}\,C_M^2$. The apparent solubility product is related to the thermodynamic solubility product by the equations governing the amount of L that may be protonated at the pH of titration and hence unavailable for precipitation, and the amount of M that may be masked by hydrolysis or complexation by other anions present. As pointed out elsewhere,[8] it is easier to use the inverse of the solubility product, which may be called the insolubility constant and treated as a stability constant for the precipitate. Ringbom's α-coefficient methods[9] are then easily applied for calculation of the minimum pH *etc* permissible, as illustrated in Fig. 1, which should be self-explanatory. Similar diagrams can be prepared to take into account masking agents.

Once the permissible pH range has been calculated from the known values of stability constants, it should be checked experimentally—stability constants are often determined under highly specialized conditions, and the values obtained may be some orders of magnitude different from those for the conditions of the titration. If the constants are not known, they must either be determined or the pH range *etc* determined empirically.

Errors are most likely to arise from co-precipitation, especially from occlusion, because digestion and other means of reducing co-precipitation are not possible in this case. A typical example is the occlusion of AgCl in the determination of iodide by argentometric titration.[10] Normally there should be an exchange reaction between AgCl and I^- to give AgI and Cl^-, but if the AgCl is occluded within AgI particles the

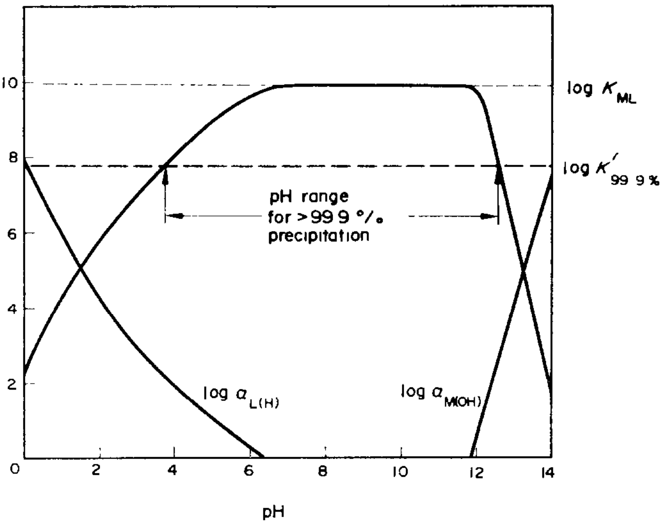


FIG. 1.—Precipitation titration of $10^{-2}M$ metal ion M with ligand H_2L, to form ML, where M forms soluble hydroxo-complexes. K_1 and K_2 for H_2L are 10^8 and 10^6 respectively, K_{sp} for ML is 10^{-10} (*i.e.*, $K_{ins} = 10^{10}$). K_3 and K_4 for $M(OH)_3^-$ and $M(OH)_4^{2-}$ are 10^6 and 10^2 respectively. $K'_{99.9\%}$ = conditional constant for at least 99.9% precipitation at the end-point.

exchange cannot take place, and there is an overconsumption of silver nitrate. The error can be eliminated by adding some ammonium carbonate to make diamminosilver(I) the effective titrant, in which case AgCl cannot precipitate. The effect of all other ions likely to be present in practical applications must therefore be checked experimentally. Precipitation reactions may sometimes be made more selective by judicious use of pH control, auxiliary masking agents, *etc*, but in general the utility of this type of reaction is severely limited by the lack of selectivity.

Further problems arise in the detection of the end-point. If a coloured precipitate is produced at the end of the main reaction, as in the Mohr method for halides, conditions must be carefully adjusted so that the overconsumption of titrant in production of a visible amount of coloured product is just compensated for by the underconsumption of titrant caused by the fact that the coloured product begins to be formed before the main reaction is entirely complete.[11] The situation may be further aggravated by the presence of ions (such as NH_4^+) which are normally thought of as harmless.[12,13] Adsorption indicators are usually fairly good, but often experience is required to recognize the end-point. Amperometric titration is often used, but the errors are seldom less than 1%, which is not surprising in view of the 1–2% error usually associated with polarographic methods. If say 10 points are used to construct the titration graph and there is an error of 2% associated with each, the overall error in assessing the end-point is likely to be about $2/\sqrt{10}\%$ or about 0.6%. In addition, it is customary to use small volumes of fairly concentrated titrant (in order to avoid excessive dilution and the need to apply a dilution correction) and the reading errors will be rather large. Potentiometric detection of the end-point is likely to prove the most satisfactory, provided that the electrodes reach potential equilibrium rapidly—otherwise the method will be too slow to be useful except for special or occasional use.

Conductimetric methods are satisfactory if the conductance can be measured sufficiently precisely (for reasons similar to those discussed for amperometric titrations) and the results are properly interpreted.

Redox reactions

The primary requirements are a means of converting the determinand into essentially the completely oxidized or reduced form, and a titrant capable of completely reducing or oxidizing the product. Obviously an excess of an auxiliary oxidant or reductant will be required in the first step, and this excess must be easily destroyed without the determinand being affected. The formal potentials for the titrant and determinand couples must be sufficiently far apart for the reaction to be at least 99·9% complete at the end-point; that means a difference of at least 0·36 V for two one-electron reactants, but only 0·09 V for a pair of two-electron reactants.

It is important to remember that the products may depend on whether a one-electron couple is matched with a one- or a two-electron couple. Hydrazine is oxidized to nitrogen by a two-electron oxidant, but to a mixture of ammonia and nitrogen by a one-electron reagent.

Examination of the Nernst equation shows that the redox potentials may be profoundly affected by changes in acidity, by complexation, and by precipitation or formation of undissociated compounds.

Effect of acidity. The most noticeable effect is on the potentials of couples involving oxy-anions that are oxidized or reduced. Typical examples are the fact that manganate is unstable in acid solution because of disproportionation, but stable in extremely alkaline solutions, and the fact that the interference of vanadium(IV) in the oxidimetric determination of iron(II) can be eliminated by making the solution $5M$ in sulphuric acid, and so raising the potential of the V(V)/V(IV) couple to a value comparable to that of the usual oxidants. Another effect is preferential protonation of one half of a couple, as for example the ferrocyanide/ferricyanide couple, or the effect of acidity on the potential of ferroin.

A further effect of changes of acidity may be on the kinetics of the reaction. As has recently been shown,[14] potassium chlorate can be used successfully as an oxidative titrant if the acidity is made high enough, though even then a catalyst is sometimes desirable as well.

Effect of complexation. It is well known that the potential of the iron couple can be shifted in either direction by use of complexing agents, the potential being increased if the iron(II) complex is more stable than the iron(III) complex (as with 1,10′-phenanthroline) and lowered if the order of stabilities is reversed (as with phosphate, fluoride, EDTA).

Effect of precipitation etc. The potential of the silver couple is decreased by introduction of an anion that forms an insoluble silver salt, the decrease being the greater the more insoluble the compound. Similarly, formation of an undissociated species such as mercuric chloride or cyanide will remove the ions of one form of the couple and hence shift the potential.

Importance of the Nernst equation. The Nernst equation not only permits calculation of the equilibrium constant (and hence the feasibility of the reaction) from the potentials of the couples involved, but also permits us to calculate the form of the potentiometric titration curve and so choose suitable indicators and decide whether other species may interfere or not by being co-titrated. It also reminds us that we cannot have an *absolutely* pure oxidant or reductant solution if the solvent is capable of redox action. It is for this reason that certain species are unstable in aqueous medium, even if protected from aerial oxidation. It further reveals that lack of thought has led to an incorrect ascription of chemical properties to certain oxidants. Many textbooks state that dichromate and ceric sulphate can be used for titrations in hydrochloric acid medium but permanganate can not. This statement is only partly true: permanganate can certainly be used, *e.g.*, for titration of antimony(III), in chloride medium. It is only unsuitable for use when the oxidation of chloride is induced by another reaction in the system, such as the oxidation of iron(II). The reason for this is that the kinetics of chloride oxidation are so slow at moderate acidities that the end-point can be detected without interference from the slow side-reaction. Unfortunately, however, many chemists read more into the statement than is there, and assume that dichromate and ceric sulphate are incapable of oxidizing chloride—an assumption that is completely false, as a practical test will readily verify.

Importance of kinetics. From what has just been said about permanganate it will be realized that the reaction kinetics may play a decisive part and override the thermodynamics. A good example is the determination of total iron in silicate rock by removal of silica by the Berzelius method, fusion of the metal oxides with pyrosulphate, dissolution in hydrochloric acid, reduction with the silver reductor, and titration with ceric sulphate, with ferroin as indicator.[15] Two difficulties arise: there is a variable blank, and the end-point "returns", that is, there is a sharp colour change followed by slow return of the reduced form of the indicator, and this behaviour is repeated on further addition of small increments of titrant. Both effects are kinetic in origin. The first arises from reduction of aerial oxygen to hydrogen peroxide in the silver reductor. The peroxide should be further reduced to water, but because the first reduction step is much faster than the second there is a build-up of peroxide, a steady state being reached because of the diffusion controlled supply of further oxygen from the air. The peroxide then reacts with iron(II) in the initiation and termination steps of the Haber-Weiss[16] mechanism for catalytic decomposition of peroxide:

$$\begin{array}{ll} Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH & \text{(initiation)} \\ Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- & \text{(termination)} \\ \left.\begin{array}{l} H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O \\ HO_2\cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH \end{array}\right\} & \text{propagation} \end{array}$$

The chain propagation steps are unlikely to have a chance to occur, since the iron is greatly in excess of the peroxide. Similar effects occur with amalgams when they are used in the presence of air.[17] The returning end-point arises because the decomposition reaction takes place in a platinum crucible and some platinum is extracted as Pt(IV) in the fusion process. According to the thermodynamics the Pt(IV) should be reduced to the metal on the silver reductor, but if the reduction is slow and occurs in two stages, *via* Pt(II), and if the residence time in the reductor column is too short (short column and/or fast flow-rate) some Pt(II) passes into the effluent and is oxidized (slowly, of course) after the preferential oxidation of the iron is complete. Fortunately the kinetics are so slow that the first sharp end-point corresponds exactly to the iron titration.[15]

Induced reactions. The Haber-Weiss mechanism just quoted is an example of an induced catalytic reaction. When such reactions can occur, they constitute a hidden source of error, which may be extremely large. In the oxidation of tin(II) with dichromate, for example, induced aerial oxidation accounts for oxidation of no less than 98% of the tin.[18] On the other hand, induced coupled reactions, in which a definite stoichiometry exists between the inductor and the acceptor systems, may be used quantitatively.

End-point detection. Indicators and potentiometry are the means usually chosen for end-point detection. Naturally the indicator potential must be matched to the equivalence point potential of the system, either by choice of indicator or by shift of a potential (*e.g.*, addition of phosphoric acid when diphenylamine is used as indicator for iron(II) oxidation). Potentiometry is satisfactory subject to the usual proviso about the speed of electrode equilibration. Spectrophotometric titration is possible if one component of the titration system has suitable absorption characteristics differing from those of the others, but if the end-point section of the curve is too rounded, dilution corrections may be necessary and are rather tedious to apply.

Complexation and acid-base reactions

The basis of these reactions is formation of a highly stable (*i.e.*, little dissociated) species such as a metal complex or water. The main criterion for successful application to titrimetry is therefore the apparent equilibrium constant for the reaction under the conditions used. In complexation reactions, if the initial metal ion concentration is C_M then for the error to be 1 ppt or less, the concentration of free metal at the end-point must be $\leqslant 10^{-3} C_M$, and this must also be the total concentration of uncomplexed titrant in the titration solution. It follows that the minimum value for the apparent stability constant of the complex is $C_M/10^{-6} C_M^2$ or $10^6/C_M$. It is therefore advisable to use fairly concentrated solutions for titration of metals that form only weak complexes. The Ringbom[9] conditional constant method can again be used to predict the minimum pH required for complete titration. It is not always recognized, however, that it is really the indicator reaction which sets the lower boundary of the permissible pH range. In the case of a weak metal-indicator complex it would be possible to find a pH at which the metal-titrant complex could be formed quantitatively while the metal-indicator complex was formed scarcely or not at all. The upper boundary of the pH range is set either by the hydrolysis characteristics of the metal ion or by the nature of the indicator. Almost all metallochromic indicators are also acid-base indicators, the colours of their metal complexes being essentially those of the species obtained on removal of one proton (sometimes more) from the indicator. For a colour change to occur at the end-point, from the colour of the metal-indicator complex to that of the free indicator, the pH must be below that at which the indicator would be deprotonated anyway. The whole system is illustrated in Fig. 2.

It is possible to achieve selectivity of complexation by pH control if the metal ions present form complexes with the titrant, with sufficiently different stability constants (Fig. 2). For ions giving complexes with similar stabilities, auxiliary masking agents are used to achieve selectivity. When the pH is adjusted it is important to remember that the buffer system must not contain ions that can act as competing ligands.[19] It is also important to remember that the buffer must have sufficient capacity to absorb the protons released during the complexation reaction.

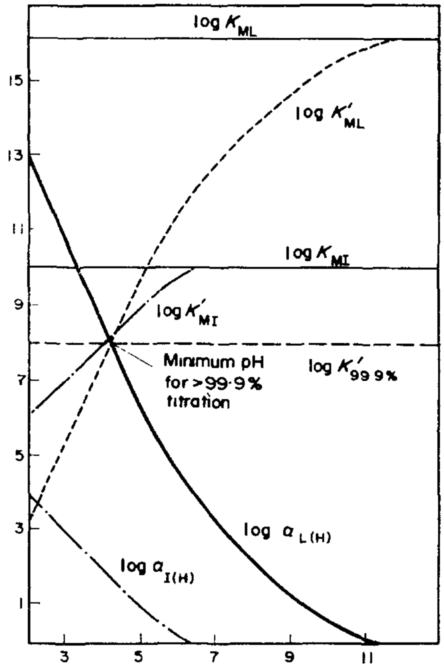


FIG. 2.—Complexation titration of $10^{-2}M$ metal ion M with ligand HL to form ML, with indicator HI. $K_{ML} = 10^{16}$; $K_{MI} = 10^{10}$; $K_{HI} = 10^{6}$; HL is EDTA. $K'_{99.9\%}$ = conditional constant for at least 99.9% completion of complexation at the end-point.

Acid-base reactions can be treated as a special case of complexation, in the simpler cases there being competition between two anions to form an undissociated species with protons. The decisive factor is the equilibrium constant for the reaction

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

$$K_{eq} = \frac{[H_2O][A^-]}{[HA][OH^-]} = \frac{K_w}{K_{HA}}$$

where

$$K_w = [H_2O]/[H^+][OH^-]; \quad K_{HA} = [HA]/[H^+][A^-]$$

If the initial concentration of acid is C_{HA}, then for 99·9% neutralization the final concentration is $10^{-3}\,C_{HA}$, and since at equilibrium [HA] = [OH$^-$], it follows that K_{eq} must be greater than $10^6/C_{HA}$ for quantitative titration ([A$^-$] will be approximately equal to C_{HA} at equivalence). If we approximate a little and use "mixed" stability constants, we can call the activity of water unity and take K_w as 10^{14}. In that case K_{HA} must be less than $K_w \cdot C_{HA}/10^6$, *i.e.*, less than $10^8\,C_{HA}$, for quantitative titration.

If the acid is weaker than this, either a larger error must be accepted or the conditions must be changed to make the acid appear to be stronger. One way of doing this is to introduce a metal ion that will form a complex with A$^-$, thus releasing protons from HA; care must be taken, however, to choose a metal ion that will not itself interfere by a hydrolysis reaction. The more common method is to change the value of K_{eq} by changing the solvent system. The use of and choice of non-aqueous solvents have been adequately discussed in various monographs[20–22] and need not be dwelt on here.

End-point detection. The most common methods for end-point detection are by means of indicators, potentiometry, spectrophotometry, conductimetry and thermometry or enthalpimetry.

In complexation reactions the indicator must of necessity form with the determinand ion a complex that is less stable than the complex formed by the determinand and titrant. If the two complexes are of comparable stability there will be an end-point error that is a function of the amount of indicator added. An example is the use of Xylenol Orange for titration of lead with EDTA. It is also essential that the indicator should not be "blocked" by the presence of other metal ions that form with it complexes more stable than the determinand-indicator complex. Adequate buffering is also necessary to prevent appearance of a false end-point by virtue of decomposition of the indicator complex by reaction with the protons released as the main reaction proceeds. It is also most important that the transition interval should be as sharp as possible. If an appreciable volume of titrant is required to traverse the end-point colour change, and two elements are being determined in the same sample by titration of the sum followed by masking of one and titration of the complexant released, there will be an error if the "sum" titration end-point is taken as appearance of the free indicator colour but the back-titration end-point is the colour of metal-indicator complex. It is essential to use the same end-point colour in both cases. The general theory of these indicators has been well covered by Ringbom.[9] The theory of acid-base indicators is well known, and it need only be stressed that the pK value of the indicator must match the pH at the equivalence point, and that adequate precautions must be taken to avoid interference by carbon dioxide in the atmosphere.

Potentiometry has already been discussed, and fortunately the glass electrode has a very rapid response and equilibration, so is ideal for potentiometric acid-base titration. The limitations of conductimetry (and amperometry) have been dealt with above and will apply here also. Spectrophotometry has been dealt with in a monograph,[23] and the theory of spectrophotometric complexation titrations adequately covered.[24,25] Thermometric and enthalpimetric methods are relatively new, but are really useful only if relatively large errors (1% or more) are acceptable. Perusal of some of the literature on these methods shows that when comparisons are made between thermometric and classical indicator methods, the errors reported for the latter are very often greatly in excess of the values that are obtainable by careful work.

Interferences. In complexation reactions, interfering ions may be dealt with by pH control or selective masking, as pointed out above. A subtle form of interference may arise, however, from the use of masking agents. It sometimes happens that a masking agent added to sequester an interfering element can act as a bridging ligand to form a mixed-metal binuclear complex with the determinand ion. If this complex happens to be inert (*i.e.*, kinetically stabilized) then the determinand ion will not react with the titrant. Such is the case with aluminium in the presence of uranyl ions and citrate.[26] Similar cases are those of copper in the presence of chromium and citrate,[27] and copper in presence of aluminium and tartrate.[28]

In acid-base reactions, the interferences are those caused by the presence of other acids or bases besides the determinand. If the strengths of the various species differ sufficiently it may be possible to titrate them consecutively, provided means of detecting the end-points are available. If the strengths are comparable, selective complexation or a change of solvent may give sufficient differentiation.

GENERAL FACTORS INFLUENCING TITRIMETRIC METHODS

Ionic strength and variations in concentration

The ionic strength can affect both the velocity and the quantitativeness of a chemical reaction, the effect being largely a function of the charges on the reacting species.[29,30] In a titration there must inevitably be a change in ionic strength in the course of the reaction, but fortunately most analytical procedures require the use of concentrations at which activity coefficients change relatively little with variation in ionic strength,[31] so it is unlikely that the ionic strength will be a serious factor. If it is, the effect can usually be "swamped" by addition of a large and constant amount of an indifferent electrolyte.

Changes in the concentration of the reactants cause a change in the reaction velocity. This is seen in the decrease in the reaction velocity near the equivalence point, a feature of practical utility (the entering stream of titrant reacts immediately in the early part of a titration, but disperses sluggishly near the end-point, so that at the point of entry the indicator has changed colour). It is therefore convenient to keep the reactant concentrations fairly constant during the preliminary investigations. Later the concentrations can be varied, especially with a view to finding the lowest concentrations that can be used satisfactorily.

Temperature

A change in temperature influences the reaction velocity and the equilibrium constant, and sometimes even the stoichiometry. Sometimes a higher temperature is used deliberately to make a slow reaction more practicable, and sometimes a very low temperature is used to make an interfering reaction so slow that its effect is nullified (so-called "kinetic masking").

Ideally, room temperature should be the optimum, but it is necessary to investigate the effect of changing the temperature because "room" temperature may vary from a few degrees in winter in Scotland to 30° or more in summer in India. High temperatures are undesirable because they may cause unfavourable effects such as decrease in stability of reactants, thermal decomposition, reaction with solvent, increasing probability of side-reactions occurring. If higher temperatures are unavoidable, a "safe" range must be found in which these undesirable effects do not occur.

Catalysis

Catalysts are sometimes added to change the reaction velocity or the mechanism of reaction, especially in redox systems. Catalysts are associated with particular reactions, and there is no general theory for prediction of which catalyst will prove convenient. Catalysts are usually found by trial and error, with the initial choice based on experience. Sometimes autocatalysis occurs, in which a reaction product itself catalyses the reaction. Induced reactions are sometimes used, but as pointed out above, unwanted ones can be a source of error.

Stability of reagents

It sometimes happens that though a titrant may be stable in aqueous solution when it is being stored, it may become less stable under the conditions used for the titration, especially if these are particularly drastic in terms of acidity or alkalinity. The effect is most likely to be observed in an indirect procedure, in which an excess of reagent must be added and the mixture left for some time for the reaction to reach completion, followed by back-titration of the excess. In such cases it is necessary to check the stability of the reagent by running a number of blank determinations with different amounts of reagent present.

Indicator solutions may not be stable on storage, especially in the case of complexometric indicators. Xylenol Orange, for example, oxidizes slowly in aqueous solution, and the oxidation product will give a coloured complex only with copper(II). The storage life of all reagents should be checked and appropriate recommendations made for their preparation.

End-point sharpness

The accuracy of a titration will be partly determined by the volume of titrant required to traverse the end-point, and on how accurately the end-point can be located within that volume. As discussed in specialist texts and articles,[32] the equivalence point may not exactly correspond to the end-point, and a correction may be necessary. The correction may be calculated or empirical. The "sharpness index" or "relative precision"[33] may be used as a means of indicating the size of the end-point error. It is essential that *some* numerical value be given for the sharpness. If indicators are used, the volume of titrant needed to give the complete colour change must be determined and reported, and if possible the colours should be described in terms of the C.I.E. indices.[34]

Other influences

Electromagnetic radiation, usually in the form of visible or ultraviolet light, can not only affect the stability of the reactants but may also participate in the reaction or accelerate or introduce side-reactions. It is therefore sometimes necessary to perform titrations under special lighting conditions, and in indirect determinations it is often necessary to keep the reaction mixture in the dark during the reaction period before the back-titration.

Ultrasonic waves have occasionally been used to affect the course of a reaction. Pressure changes, though often used in technology, are not used in titrations, because of the experimental complications introduced.

RESULTS AND APPLICATIONS

Once the method has been worked out, it is necessary to validate it by standardization, and by application to standard samples containing the species of interest. The standardization is customarily done by preparing a standard solution of known concentration and titrating equal portions of it. In our opinion this is not a sound practice. First, all measurements are made by volume, and as discussed by Conway,[35] it is then necessary to calibrate all apparatus used, so that the personal error may be assessed. Secondly, once the first titration has been done, the tendency is to add rapidly almost the required volume of titrant to the second sample and only the last few drops are added slowly. The result is a variable drainage error, if a normal gravity-feed burette is used.[35] Furthermore, if fractions of a division are estimated in reading the burette, there is an unconscious urge to make the readings agree as closely as possible. It is much more reliable to make up the standard solution by weight and to take different weight fractions of it. Each titration must then be done more or less individually without reference to the others (unless the operator is unable to resist doing mental arithmetic), and the error in the amount of sample taken will be virtually eliminated. If a sufficiently wide range of sample weights is taken, a plot of "taken" against "found" will reveal any bias in the results, and the existence of any "blank" correction. Repetition of the procedure in the presence of the other elements expected to occur in any applications will reveal the extent of any interference by these species. The concentration ratios used must be realistic.[3]

Finally, the method must be applied to standard samples of the materials for which it is suitable, and the results compared statistically with those obtained by the best previously existing methods. It is essential to have enough replicate determinations to make the statistics meaningful, and the Snedecor *F*-test or "Student's" *t* should be applied as a criterion of significant improvement.[36]

PUBLICATION OF RESULTS

If the work has been successful, then in the preparation of a paper for publication it is necessary to report on all the features dealt with above. In particular, attention must be paid to the following points.

1. Stability of reagents, and special precautions to be taken in their preparation and storage.
2. Standardization of reagents and calibration of apparatus, with details given of the errors actually obtained.
3. Proof of the stoichiometry, and establishment of the tolerance ranges[37] for concentrations of reactants, interferents, and other species necessarily present.
4. The speed of the reaction, especially with regard to end-point detection and to the standing time in the case of indirect determinations.
5. The nature of the end-point detection, with specification of sharpness of any colour changes, details of indicator corrections or other end-point corrections. In cases of "dead-stop" methods *etc*, the response time of the indicating system should be expressed in terms of amount of titrant added, if the titrant is being added automatically or generated electrolytically. In coulometric work the current efficiency must be determined, and the timing error should be established and reported.
6. In description of the procedure, all tolerances on amounts of reagents should be clearly stated, and any special precautions stated.[37]
7. There must be adequate validation of results, supported by statistical analysis.
8. Applications of the method must be proposed and at least some of them validated experimentally. There must be a proper comparison with existing methods.
9. If possible, the method should be tested by someone who has not used it before, and *those* results quoted as well.

Résumé—On a établi les conditions nécessaires pour le développement de méthodes titrimétriques et pour la rédaction du travail pour publication. On discute des principes généraux de divers types de réaction de titrage, et l'on prête particulièrement attention aux paramètres qui influent sur les réactions chimiques.

Zusammenfassung—Die Anforderungen an die Ausarbeitung titrimetrischer Methoden und an zu publizierende Manuskripte mit solchen Themen werden aufgeführt. Die allgemeinen Grundlagen für verschiedene Typen von Titrationsreaktionen werden erörtert und dabei besonderes Gewicht auf die Parameter gelegt, die chemische Reaktionen beeinflussen.

REFERENCES

1. H. Beckurts, *Massanalyse*, Vieweg Verlag, Braunschweig, 1913.
2. G. F. Kirkbright, *Talanta*, 1966, **13**, 1.
3. L. Erdey, L. Polós and R. A. Chalmers, *ibid.*, 1970, **17**, 1143.
4. G. E. F. Lundell, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 221.
5. F. Penny, *Chem. Gaz.*, 1850, **8**, 330.
6. F. Margueritte, *Compt. Rend.*, 1846, **22**, 587.
7. *e.g.*, K. Sriraman, *Talanta*, 1971, **18**, 361.
8. R. A. Chalmers, *Aspects of Analytical Chemistry*, Oliver and Boyd, Edinburgh, 1968.
9. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1964.
10. I. M. Kolthoff, *Z. Anal. Chem.*, 1927, **70**, 395 (see also K. Fajans and O. Hassel, *Z. Electrochem.*, 1923, **29**, 495).
11. R. Belcher, A. M. G. Macdonald and E. Parry, *Anal. Chim. Acta*, 1957, **16**, 524.
12. J. Block and O. B. Waters, *Talanta*, 1967, **14**, 1130.
13. E. Wànninen, *ibid.*, 1968, **15**, 717.
14. C. R. Murty and G. G. Rao, *ibid.*, 1972, **19**, 45.
15. R. A. Chalmers and C. C. Miller, *Analyst*, 1952, **77**, 2.
16. F. Haber and J. Weiss, *Naturwissen.*, 1932, **20**, 948; *Proc. Roy. Soc.*, 1934, **A147**, 332.
17. R. A. Chalmers, D. E. Edmond and W. Moser, *Anal. Chim. Acta*, 1966, **35**, 404.
18. E. Lenssen and J. Löwenthal, *J. Prakt. Chem.*, 1862, **87**, 193.
19. A. Ringbom, *op. cit.*, p. 93.
20. W. Huber, *Titrations in Non-Aqueous Solvents*, Academic Press, New York, 1967.
21. I. Kucharský and L. Šafařík, *Titrations in Non-Aqueous Solvents*, Elsevier, London, 1965.
22. I. Gyenes, *Titration in Non-Aqueous Media*, Iliffe, London, 1967.
23. J. B. Headridge, *Photometric Titrations*, 2nd Ed., Pergamon, Oxford, 1961.
24. J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, 1954, **10**, 356.
25. H. Flaschka and S. Khalafalla, *Z. Anal. Chem.*, 1957, **156**, 401.
26. G. L. Boorman and W. B. Holbrook, *Anal. Chem.*, 1959, **31**, 10.
27. H. M. N. H. Irving and W. R. Tomlinson, *Talanta*, 1968, **15**, 1267.
28. H. Flaschka, J. Butcher and R. Speights, *ibid.*, 1961, **8**, 400.
29. J. C. Jungers, *Cinétique chimique appliquée*, Societé des Éditions Technic, Paris, 1958.
30. R. Brdička, *Grundlagen der physikalischen Chemie*, Deutscher Verlag der Wissenschaften, Berlin, 1963.
31. A. Ringbom, *op. cit.*, p. 24.
32. *e.g.*, H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, New York, 1960.
    E. Bishop, in *Comprehensive Analytical Chemistry*, Vol. 1B (eds. C. L. Wilson and D. W. Wilson), Elsevier, Amsterdam, 1960.
33. A. A. Benedetti-Pichler, *Essentials of Quantitative Analysis*, Ronald Press, New York, 1956.
34. *e.g.*, S. Kotrlý and K. Vytřas, *Talanta*, 1971, **18**, 253.
35. E. J. Conway, *Micro-Diffusion Analysis and Volumetric Error*, Crosby Lockwood, London, 1947.
36. K. Eckschlager, *Errors, Measurements and Results in Chemical Analysis*, pp. 111 and 118. Van Nostrand Reinhold, London, 1969.
37. A. L. Wilson, *Talanta*, 1970, **17**, 21, 31.

Talanta, 1972, Vol. 19, pp. 747 to 760. Pergamon Press. Printed in Northern Ireland

DEVELOPMENT AND PUBLICATION OF NEW TITRIMETRIC METHODS

A. BERKA and J. ŠEVČÍK
Department of Analytical Chemistry, Charles University,
Prague 2, Albertov 2030, Czechoslovakia

ROBERT A. CHALMERS
Chemistry Department, University of Aberdeen, Old Aberdeen,
Scotland

(*Received* 30 *April* 1970. *Revised* 10 *August* 1971. *Accepted* 20 *November* 1971)

Summary—Requirements are laid down for the development of titrimetric methods and for writing up the work for publication. The general principles of various types of titration reaction are discussed, and special attention is paid to the parameters which influence chemical reactions.

ALTHOUGH about 200 years have elapsed since the publication of the first papers dealing with titrimetric analysis,[1] the technique is still as widely used as ever, especially since the development of physicochemical methods of measurement, which permit not only objective detection of the end-point of a titration but also monitoring of the course of the reaction and hence a better understanding of its chemistry. Better understanding in turn leads to improvements in speed, precision, accuracy, sensitivity and/or selectivity of the procedures. In spite of all this, however, many methods are published which leave much to be desired both in their usefulness and in validation of the conditions used. It may be argued that that is the fault of the editors and referees concerned, but it is not really part of their duties to give private tuition in research methods. This paper has therefore been added to those already published on how to develop and write up methods,[2,3] with the intention of fulfilling the need for such instruction.

GENERAL REQUIREMENTS OF A TITRIMETRIC METHOD

In general, as with other analytical methods, titrimetric procedures should be accurate and precise, simple to use, work under a wide range of conditions, fulfil a definite need and have practical applications (otherwise they are merely academic exercises and of little value) and should be rapid (if they are slow they offer no advantage over gravimetric methods). Some of these criteria are worth further comment. By "accurate and precise" we mean that the results should be correct and reproducible within the limits set by the random errors in measurement, and in the research work on a new method it is imperative that the errors be kept as small as possible. If it is known that a method is capable of giving results correct to within 1 part per thousand (1 ppt) then if a larger error is acceptable for some particular application, the method can be used with confidence even if less care is taken. On the other hand, if the best that can be done with a method gives an error of 1%, application of that method is limited to those situations in which a larger error than this can be tolerated. All too often there seems to be a failure to realise that in titrimetry the need to standardize the titrant introduces an additional source of error, since any mistake made in determining the titre will cause a bias in all the results obtained with the titrant. Consider, for example, the standardization of ceric sulphate with arsenious oxide, with osmium tetroxide as catalyst and ferroin as indicator. To give a reasonable titration volume of $0.1M$ ceric sulphate (*i.e.*, about 30 ml, which can be measured with a reading error of about 0.03 ml or less if care is taken), a weight of about 150 mg of arsenious oxide is required. Suppose this is weighed on a normal fourth-place balance with a standard deviation of 0.05 mg at the weight loading used, and that the balance weights have not been calibrated. The random error in weighing by difference will be about 0.15 mg (95% confidence limits) and in addition there may be a biased error from the unknown errors in the weights. The manufacturer's tolerance on weights up to 500 mg is 0·05 mg, and since there must be an exchange of at least two fractional weights it would be possible for this bias to amount to at least 0·1 mg. If this reinforces the random error, we have already an error of nearly 2 ppt in the weight of primary standard taken, plus an expected reading error of 1 ppt. In addition there is the end-point error arising from the fact that we do not know how much of the last increment added was actually required to reach the end-point and how much was excess. "Splitting" drops is tedious, and this error can be minimized by assuming that the end-point was reached on addition of half the last drop. The error is then only half the drop-size. If a varying amount of indicator is added to replicate samples, there will be a variation in the amount of titrant needed to oxidize the indicator, and if the indicator is too concentrated or too large an amount is added (or both!) another biased error can occur. Obviously care and thought are needed to measure the titre to within 1 ppt, and if the standardization is not done accurately, the results of use of the titrant will not be as meaningful as they should be. How often we see in a paper the statement that a solution was standardized by some method or other, usually described only by a reference, and no information is given as to the precision of the results obtained. Similar remarks apply to calibration of apparatus, for which the results are scarcely ever given.

By "simple to use" and "work under a wide range of conditions" we mean that there should be as few procedural steps as possible, since each can lead to a mistake being made, and that tolerances on such factors as pH range, ionic strength, amounts of particular compounds permitted to be present, should be as wide as possible, so that undue care need not be taken over adjustment of conditions. A procedure that requires very close control of pH is not nearly as satisfactory to use as one that operates over a pH range of several units.

By "rapid" we mean that reaction should proceed more rapidly than titrant can be added to the system, or at least very nearly so. A procedure in which a wait of several minutes is necessary between additions of titrant is going to be a very irksome one to use, and not at all suitable for routine analysis. Many potentiometric systems suffer from this drawback, when the electrode system used takes some time to reach a stable potential as the titration proceeds. Sometimes, of course, a slow reaction can be combined with a back-titration that is rapid, by adding an excess of reactant, leaving it for a sufficient time, and then titrating the excess. Again, an interfering reaction may be made to occur so slowly that it does not affect the main reaction, or the kinetics may already be sufficiently different for no interference to occur.

By "fulfilling a need and having practical application" we mean that a reaction that is suitable only for analysis of a pure solution of the substance to be determined is of such limited usefulness as to be practically worthless unless it is so very much better than any other available method that it is necessarily the method of choice for standardizing solutions of that substance. This was stated very clearly over 30 years ago by Lundell in his paper "Analysis of Things as They Are",[4] a paper that should be compulsory reading for all analytical chemists. The literature is full of "new and improved" methods that are in fact poorer in performance than the ones they seek to replace, and that are often based on standardizations performed by means of methods that they criticize and claim to supplant. Many methods have been published for the titrimetric determination of iron, but very few of them are better than the earliest methods of all—oxidation of iron(II) with dichromate[5] or permanganate.[6]

Unless the method being developed promises to fulfill these criteria, it seems scarcely worth while pursuing it. If it *does* show promise, however, there must be a proper investigation of the conditions under which it should be used, and a proper assessment of its scope of application and of its reliability. The remainder of this paper will deal with these aspects. Each type of reaction will be dealt with separately, as will standardization and end-point detection.

BASIC CONDITIONS OF TITRIMETRIC DETERMINATIONS

Only those reactions which proceed in stoichiometric ratio in a chosen solvent, without side-reactions and consecutive reactions, can serve as a basis for titrimetric determinations. The end-point of the reaction must be detectable by chemical or physical means.

Special demands are made of the substance used as titrant. It must be of well defined composition, easily soluble in the chosen solvent so that solutions covering a wide range of concentration can be prepared, and its solutions should either be stable or easily standardized. Some titrants which are unstable because of reactions with the solvent or the atmosphere, or because of volatility or light-sensitivity, can still be used if the active species is generated *in situ* electrolytically. It is desirable that the substance should be readily available.

Although a detailed study of the kinetics is not essential for development of a titrimetric method, it stands to reason that a method that is kinetically slow is not a very useful one, especially for routine work. However, slow reactions may be used in indirect methods if the back-titration reaction is fast. On the other hand, a competing reaction may be suppressed by proper adjustment of the conditions if its rate of reaction is much slower than that of the main reaction. Similarly it is not essential that the mechanism of the reaction be known, though again, knowledge of it may be useful in certain circumstances. The stoichiometry can be expressed in terms of equivalents or of the ratio of molar concentrations, which should be a ratio between small integers. It is worth stating at this point that in titrimetry it is essential to retain both the mole-concept and the concept of normality. Each has its own special field of application, together with an enormous overlap of applicability, where either can be used. For example, in dealing with polymers and many biochemical systems, it is not known (or cannot be known) what the molecular weight is, although it is perfectly easy to determine the number of equivalents of some reactive group in a given weight of sample. In contrast, normality is meaningless in complexation reactions. For the rest, the objection to the use of equivalents, *viz.* that a different equivalent weight must be used for different reactions of the same substance, is just as much an objection to the use of moles, because the equation must be written down in both cases, and the only real difference is in the point at which the stoichiometric coefficients are introduced into the calculation. If the equivalent is defined as that weight of material which will react with one mole of hydrogen ions or of electrons or with one equivalent of any other substance, both conventions are referred unambiguously to the mole concept, and there should be no difficulty in understanding and applying both.

Assumptions about stoichiometry are best verified by using equimolar solutions of the titrant and titrand and seeing whether the volumes needed to complete the reaction are in some simple whole-number ratio. If they are not, then either the reaction is non-quantitative for kinetic or thermodynamic reasons, or the main reaction is accompanied by side-reactions or consecutive reactions. Because these latter reactions can proceed at a considerably lower velocity than the main reaction, it is convenient to add an excess of titrant and to determine the amount unreacted after a sufficient time, to verify that there is no consecutive reaction. The stoichiometry can also be checked by quantitative determination of the reaction products. In direct titrations (see below), a titration error can be falsely attributed to non-quantitative reaction if the stoichiometry is not checked. It is often difficult, however, to decide whether non-quantitative results are due to the kinetics or the thermodynamics.[7]

Precipitation reactions

The main criterion is the value of the solubility product for the substance being precipitated. If C_M is the initial concentration of the metal to be precipitated by the titrant, then for 1 ppt error (which we will take as the working error to be aimed at) the final concentration must be $10^{-3}\ C_M$, and for a precipitate ML the apparent solubility product must be $10^{-6}\ C_M^2$. The apparent solubility product is related to the thermodynamic solubility product by the equations governing the amount of L that may be protonated at the pH of titration and hence unavailable for precipitation, and the amount of M that may be masked by hydrolysis or complexation by other anions present. As pointed out elsewhere,[8] it is easier to use the inverse of the solubility product, which may be called the insolubility constant and treated as a stability constant for the precipitate. Ringbom's α-coefficient methods[9] are then easily applied for calculation of the minimum pH *etc* permissible, as illustrated in Fig. 1, which should be self-explanatory. Similar diagrams can be prepared to take into account masking agents.

Once the permissible pH range has been calculated from the known values of stability constants, it should be checked experimentally—stability constants are often determined under highly specialized conditions, and the values obtained may be some orders of magnitude different from those for the conditions of the titration. If the constants are not known, they must either be determined or the pH range *etc* determined empirically.

Errors are most likely to arise from co-precipitation, especially from occlusion, because digestion and other means of reducing co-precipitation are not possible in this case. A typical example is the occlusion of AgCl in the determination of iodide by argentometric titration.[10] Normally there should be an exchange reaction between AgCl and I^- to give AgI and Cl^-, but if the AgCl is occluded within AgI particles the

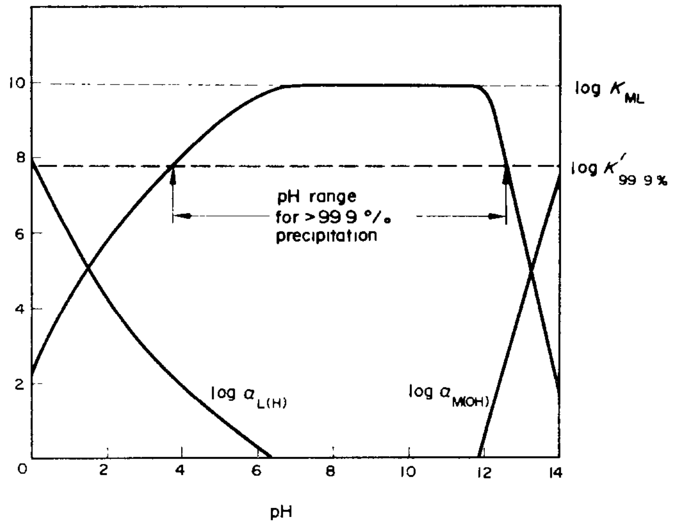


FIG. 1.—Precipitation titration of $10^{-2}M$ metal ion M with ligand H_2L, to form ML, where M forms soluble hydroxo-complexes. K_1 and K_2 for H_2L are 10^2 and 10^6 respectively, K_{sp} for ML is 10^{-10} (*i.e.*, $K_{ins} = 10^{10}$). K_3 and K_4 for $M(OH)_3^-$ and $M(OH)_4^{2-}$ are 10^6 and 10^2 respectively. $K'_{99.9\%}$ = conditional constant for at least 99.9% precipitation at the end-point.

exchange cannot take place, and there is an overconsumption of silver nitrate. The error can be eliminated by adding some ammonium carbonate to make diamminosilver(I) the effective titrant, in which case AgCl cannot precipitate. The effect of all other ions likely to be present in practical applications must therefore be checked experimentally. Precipitation reactions may sometimes be made more selective by judicious use of pH control, auxiliary masking agents, *etc*, but in general the utility of this type of reaction is severely limited by the lack of selectivity.

Further problems arise in the detection of the end-point. If a coloured precipitate is produced at the end of the main reaction, as in the Mohr method for halides, conditions must be carefully adjusted so that the overconsumption of titrant in production of a visible amount of coloured product is just compensated for by the underconsumption of titrant caused by the fact that the coloured product begins to be formed before the main reaction is entirely complete.[11] The situation may be further aggravated by the presence of ions (such as NH_4^+) which are normally thought of as harmless.[12,13] Adsorption indicators are usually fairly good, but often experience is required to recognize the end-point. Amperometric titration is often used, but the errors are seldom less than 1%, which is not surprising in view of the 1–2% error usually associated with polarographic methods. If say 10 points are used to construct the titration graph and there is an error of 2% associated with each, the overall error in assessing the end-point is likely to be about $2/\sqrt{10}\%$ or about 0.6%. In addition, it is customary to use small volumes of fairly concentrated titrant (in order to avoid excessive dilution and the need to apply a dilution correction) and the reading errors will be rather large. Potentiometric detection of the end-point is likely to prove the most satisfactory, provided that the electrodes reach potential equilibrium rapidly—otherwise the method will be too slow to be useful except for special or occasional use.

Conductimetric methods are satisfactory if the conductance can be measured sufficiently precisely (for reasons similar to those discussed for amperometric titrations) and the results are properly interpreted.

Redox reactions

The primary requirements are a means of converting the determinand into essentially the completely oxidized or reduced form, and a titrant capable of completely reducing or oxidizing the product. Obviously an excess of an auxiliary oxidant or reductant will be required in the first step, and this excess must be easily destroyed without the determinand being affected. The formal potentials for the titrant and determinand couples must be sufficiently far apart for the reaction to be at least 99·9% complete at the end-point; that means a difference of at least 0·36 V for two one-electron reactants, but only 0·09 V for a pair of two-electron reactants.

It is important to remember that the products may depend on whether a one-electron couple is matched with a one- or a two-electron couple. Hydrazine is oxidized to nitrogen by a two-electron oxidant, but to a mixture of ammonia and nitrogen by a one-electron reagent.

Examination of the Nernst equation shows that the redox potentials may be profoundly affected by changes in acidity, by complexation, and by precipitation or formation of undissociated compounds.

Effect of acidity. The most noticeable effect is on the potentials of couples involving oxy-anions that are oxidized or reduced. Typical examples are the fact that manganate is unstable in acid solution because of disproportionation, but stable in extremely alkaline solutions, and the fact that the interference of vanadium(IV) in the oxidimetric determination of iron(II) can be eliminated by making the solution 5*M* in sulphuric acid, and so raising the potential of the V(V)/V(IV) couple to a value comparable to that of the usual oxidants. Another effect is preferential protonation of one half of a couple, as for example the ferrocyanide/ferricyanide couple, or the effect of acidity on the potential of ferroin.

A further effect of changes of acidity may be on the kinetics of the reaction. As has recently been shown,[14] potassium chlorate can be used successfully as an oxidative titrant if the acidity is made high enough, though even then a catalyst is sometimes desirable as well.

Effect of complexation. It is well known that the potential of the iron couple can be shifted in either direction by use of complexing agents, the potential being increased if the iron(II) complex is more stable than the iron(III) complex (as with 1,10′-phenanthroline) and lowered if the order of stabilities is reversed (as with phosphate, fluoride, EDTA).

Effect of precipitation etc. The potential of the silver couple is decreased by introduction of an anion that forms an insoluble silver salt, the decrease being the greater the more insoluble the compound. Similarly, formation of an undissociated species such as mercuric chloride or cyanide will remove the ions of one form of the couple and hence shift the potential.

Importance of the Nernst equation. The Nernst equation not only permits calculation of the equilibrium constant (and hence the feasibility of the reaction) from the potentials of the couples involved, but also permits us to calculate the form of the potentiometric titration curve and so choose suitable indicators and decide whether other species may interfere or not by being co-titrated. It also reminds us that we cannot have an *absolutely* pure oxidant or reductant solution if the solvent is capable of redox action. It is for this reason that certain species are unstable in aqueous medium, even if protected from aerial oxidation. It further reveals that lack of thought has led to an incorrect ascription of chemical properties to certain oxidants. Many textbooks state that dichromate and ceric sulphate can be used for titrations in hydrochloric acid medium but permanganate can not. This statement is only partly true: permanganate can certainly be used, *e.g.*, for titration of antimony(III), in chloride medium. It is only unsuitable for use when the oxidation of chloride is induced by another reaction in the system, such as the oxidation of iron(II). The reason for this is that the kinetics of chloride oxidation are so slow at moderate acidities that the end-point can be detected without interference from the slow side-reaction. Unfortunately, however, many chemists read more into the statement than is there, and assume that dichromate and ceric sulphate are incapable of oxidizing chloride—an assumption that is completely false, as a practical test will readily verify.

Importance of kinetics. From what has just been said about permanganate it will be realized that the reaction kinetics may play a decisive part and override the thermodynamics. A good example is the determination of total iron in silicate rock by removal of silica by the Berzelius method, fusion of the metal oxides with pyrosulphate, dissolution in hydrochloric acid, reduction with the silver reductor, and titration with ceric sulphate, with ferroin as indicator.[15] Two difficulties arise: there is a variable blank, and the end-point "returns", that is, there is a sharp colour change followed by slow return of the reduced form of the indicator, and this behaviour is repeated on further addition of small increments of titrant. Both effects are kinetic in origin. The first arises from reduction of aerial oxygen to hydrogen peroxide in the silver reductor. The peroxide should be further reduced to water, but because the first reduction step is much faster than the second there is a build-up of peroxide, a steady state being reached because of the diffusion controlled supply of further oxygen from the air. The peroxide then reacts with iron(II) in the initiation and termination steps of the Haber-Weiss[16] mechanism for catalytic decomposition of peroxide:

$$\begin{aligned}
&Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad \text{(initiation)}\\
&Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad \text{(termination)}\\
&\left.\begin{aligned}&H_2O_2 + \cdot OH \rightarrow HO_2\cdot + H_2O\\ &HO_2\cdot + H_2O_2 \rightarrow H_2O + O_2 + \cdot OH\end{aligned}\right\}\text{propagation}
\end{aligned}$$

The chain propagation steps are unlikely to have a chance to occur, since the iron is greatly in excess of the peroxide. Similar effects occur with amalgams when they are used in the presence of air.[17] The returning end-point arises because the decomposition reaction takes place in a platinum crucible and some platinum is extracted as Pt(IV) in the fusion process. According to the thermodynamics the Pt(IV) should be reduced to the metal on the silver reductor, but if the reduction is slow and occurs in two stages, *via* Pt(II), and if the residence time in the reductor column is too short (short column and/or fast flow-rate) some Pt(II) passes into the effluent and is oxidized (slowly, of course) after the preferential oxidation of the iron is complete. Fortunately the kinetics are so slow that the first sharp end-point corresponds exactly to the iron titration.[15]

Induced reactions. The Haber-Weiss mechanism just quoted is an example of an induced catalytic reaction. When such reactions can occur, they constitute a hidden source of error, which may be extremely large. In the oxidation of tin(II) with dichromate, for example, induced aerial oxidation accounts for oxidation of no less than 98% of the tin.[18] On the other hand, induced coupled reactions, in which a definite stoichiometry exists between the inductor and the acceptor systems, may be used quantitatively.

End-point detection. Indicators and potentiometry are the means usually chosen for end-point detection. Naturally the indicator potential must be matched to the equivalence point potential of the system, either by choice of indicator or by shift of a potential (*e.g.*, addition of phosphoric acid when diphenylamine is used as indicator for iron(II) oxidation). Potentiometry is satisfactory subject to the usual proviso about the speed of electrode equilibration. Spectrophotometric titration is possible if one component of the titration system has suitable absorption characteristics differing from those of the others, but if the end-point section of the curve is too rounded, dilution corrections may be necessary and are rather tedious to apply.

Complexation and acid-base reactions

The basis of these reactions is formation of a highly stable (*i.e.*, little dissociated) species such as a metal complex or water. The main criterion for successful application to titrimetry is therefore the apparent equilibrium constant for the reaction under the conditions used. In complexation reactions, if the initial metal ion concentration is C_M then for the error to be 1 ppt or less, the concentration of free metal at the end-point must be $\leqslant 10^{-3}\, C_M$, and this must also be the total concentration of uncomplexed titrant in the titration solution. It follows that the minimum value for the apparent stability constant of the complex is $C_M/10^{-6}\, C_M^2$ or $10^6/C_M$. It is therefore advisable to use fairly concentrated solutions for titration of metals that form only weak complexes. The Ringbom[9] conditional constant method can again be used to predict the minimum pH required for complete titration. It is not always recognized, however, that it is really the indicator reaction which sets the lower boundary of the permissible pH range. In the case of a weak metal-indicator complex it would be possible to find a pH at which the metal-titrant complex could be formed quantitatively while the metal-indicator complex was formed scarcely or not at all. The upper boundary of the pH range is set either by the hydrolysis characteristics of the metal ion or by the nature of the indicator. Almost all metallochromic indicators are also acid-base indicators, the colours of their metal complexes being essentially those of the species obtained on removal of one proton (sometimes more) from the indicator. For a colour change to occur at the end-point, from the colour of the metal-indicator complex to that of the free indicator, the pH must be below that at which the indicator would be deprotonated anyway. The whole system is illustrated in Fig. 2.

It is possible to achieve selectivity of complexation by pH control if the metal ions present form complexes with the titrant, with sufficiently different stability constants (Fig. 2). For ions giving complexes with similar stabilities, auxiliary masking agents are used to achieve selectivity. When the pH is adjusted it is important to remember that the buffer system must not contain ions that can act as competing ligands.[19] It is also important to remember that the buffer must have sufficient capacity to absorb the protons released during the complexation reaction.

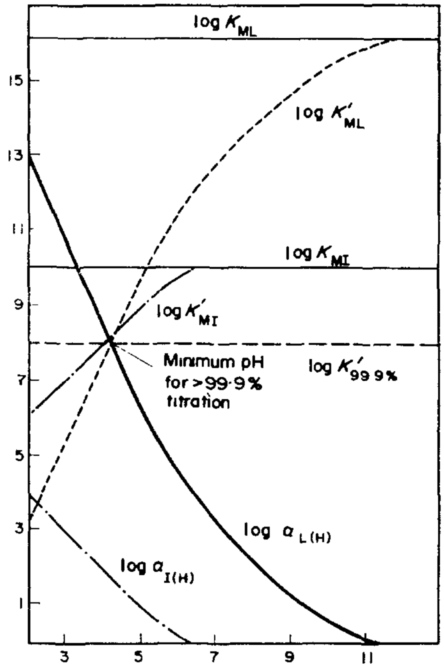


FIG. 2.—Complexation titration of $10^{-2}M$ metal ion M with ligand HL to form ML, with indicator HI. $K_{ML} = 10^{16}$; $K_{MI} = 10^{10}$; $K_{HI} = 10^{6}$; HL is EDTA. $K'_{99.9\%}$ = conditional constant for at least 99.9% completion of complexation at the end-point.

Acid-base reactions can be treated as a special case of complexation, in the simpler cases there being competition between two anions to form an undissociated species with protons. The decisive factor is the equilibrium constant for the reaction

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

$$K_{eq} = \frac{[H_2O][A^-]}{[HA][OH^-]} = \frac{K_w}{K_{HA}}$$

where

$$K_w = [H_2O]/[H^+][OH^-]; \quad K_{HA} = [HA]/[H^+][A^-]$$

If the initial concentration of acid is C_{HA}, then for 99·9% neutralization the final concentration is $10^{-3}\,C_{HA}$, and since at equilibrium [HA] = [OH⁻], it follows that K_{eq} must be greater than $10^6/C_{HA}$ for quantitative titration ($[A^-]$ will be approximately equal to C_{HA} at equivalence). If we approximate a little and use "mixed" stability constants, we can call the activity of water unity and take K_w as 10^{14}. In that case K_{HA} must be less than $K_w \cdot C_{HA}/10^6$, *i.e.*, less than $10^8\,C_{HA}$, for quantitative titration.

If the acid is weaker than this, either a larger error must be accepted or the conditions must be changed to make the acid appear to be stronger. One way of doing this is to introduce a metal ion that will form a complex with A^-, thus releasing protons from HA; care must be taken, however, to choose a metal ion that will not itself interfere by a hydrolysis reaction. The more common method is to change the value of K_{eq} by changing the solvent system. The use of and choice of non-aqueous solvents have been adequately discussed in various monographs[20–22] and need not be dwelt on here.

End-point detection. The most common methods for end-point detection are by means of indicators, potentiometry, spectrophotometry, conductimetry and thermometry or enthalpimetry.

In complexation reactions the indicator must of necessity form with the determinand ion a complex that is less stable than the complex formed by the determinand and titrant. If the two complexes are of comparable stability there will be an end-point error that is a function of the amount of indicator added. An example is the use of Xylenol Orange for titration of lead with EDTA. It is also essential that the indicator should not be "blocked" by the presence of other metal ions that form with it complexes more stable than the determinand-indicator complex. Adequate buffering is also necessary to prevent appearance of a false end-point by virtue of decomposition of the indicator complex by reaction with the protons released as the main reaction proceeds. It is also most important that the transition interval should be as sharp as possible. If an appreciable volume of titrant is required to traverse the end-point colour change, and two elements are being determined in the same sample by titration of the sum followed by masking of one and titration of the complexant released, there will be an error if the "sum" titration end-point is taken as appearance of the free indicator colour but the back-titration end-point is the colour of metal-indicator complex. It is essential to use the same end-point colour in both cases. The general theory of these indicators has been well covered by Ringbom.[9] The theory of acid-base indicators is well known, and it need only be stressed that the pK value of the indicator must match the pH at the equivalence point, and that adequate precautions must be taken to avoid interference by carbon dioxide in the atmosphere.

Potentiometry has already been discussed, and fortunately the glass electrode has a very rapid response and equilibration, so is ideal for potentiometric acid-base titration. The limitations of conductimetry (and amperometry) have been dealt with above and will apply here also. Spectrophotometry has been dealt with in a monograph,[23] and the theory of spectrophotometric complexation titrations adequately covered.[24,25] Thermometric and enthalpimetric methods are relatively new, but are really useful only if relatively large errors (1% or more) are acceptable. Perusal of some of the literature on these methods shows that when comparisons are made between thermometric and classical indicator methods, the errors reported for the latter are very often greatly in excess of the values that are obtainable by careful work.

Interferences. In complexation reactions, interfering ions may be dealt with by pH control or selective masking, as pointed out above. A subtle form of interference may arise, however, from the use of masking agents. It sometimes happens that a masking agent added to sequester an interfering element can act as a bridging ligand to form a mixed-metal binuclear complex with the determinand ion. If this complex happens to be inert (*i.e.*, kinetically stabilized) then the determinand ion will not react with the titrant. Such is the case with aluminium in the presence of uranyl ions and citrate.[26] Similar cases are those of copper in the presence of chromium and citrate,[27] and copper in presence of aluminium and tartrate.[28]

In acid-base reactions, the interferences are those caused by the presence of other acids or bases besides the determinand. If the strengths of the various species differ sufficiently it may be possible to titrate them consecutively, provided means of detecting the end-points are available. If the strengths are comparable, selective complexation or a change of solvent may give sufficient differentiation.

GENERAL FACTORS INFLUENCING TITRIMETRIC METHODS

Ionic strength and variations in concentration

The ionic strength can affect both the velocity and the quantitativeness of a chemical reaction, the effect being largely a function of the charges on the reacting species.[29,30] In a titration there must inevitably be a change in ionic strength in the course of the reaction, but fortunately most analytical procedures require the use of concentrations at which activity coefficients change relatively little with variation in ionic strength,[31] so it is unlikely that the ionic strength will be a serious factor. If it is, the effect can usually be "swamped" by addition of a large and constant amount of an indifferent electrolyte.

Changes in the concentration of the reactants cause a change in the reaction velocity. This is seen in the decrease in the reaction velocity near the equivalence point, a feature of practical utility (the entering stream of titrant reacts immediately in the early part of a titration, but disperses sluggishly near the end-point, so that at the point of entry the indicator has changed colour). It is therefore convenient to keep the reactant concentrations fairly constant during the preliminary investigations. Later the concentrations can be varied, especially with a view to finding the lowest concentrations that can be used satisfactorily.

Temperature

A change in temperature influences the reaction velocity and the equilibrium constant, and sometimes even the stoichiometry. Sometimes a higher temperature is used deliberately to make a slow reaction more practicable, and sometimes a very low temperature is used to make an interfering reaction so slow that its effect is nullified (so-called "kinetic masking").

Ideally, room temperature should be the optimum, but it is necessary to investigate the effect of changing the temperature because "room" temperature may vary from a few degrees in winter in Scotland to 30° or more in summer in India. High temperatures are undesirable because they may cause unfavourable effects such as decrease in stability of reactants, thermal decomposition, reaction with solvent, increasing probability of side-reactions occurring. If higher temperatures are unavoidable, a "safe" range must be found in which these undesirable effects do not occur.

Catalysis

Catalysts are sometimes added to change the reaction velocity or the mechanism of reaction, especially in redox systems. Catalysts are associated with particular reactions, and there is no general theory for prediction of which catalyst will prove convenient. Catalysts are usually found by trial and error, with the initial choice based on experience. Sometimes autocatalysis occurs, in which a reaction product itself catalyses the reaction. Induced reactions are sometimes used, but as pointed out above, unwanted ones can be a source of error.

Stability of reagents

It sometimes happens that though a titrant may be stable in aqueous solution when it is being stored, it may become less stable under the conditions used for the titration, especially if these are particularly drastic in terms of acidity or alkalinity. The effect is most likely to be observed in an indirect procedure, in which an excess of reagent must be added and the mixture left for some time for the reaction to reach completion, followed by back-titration of the excess. In such cases it is necessary to check the stability of the reagent by running a number of blank determinations with different amounts of reagent present.

Indicator solutions may not be stable on storage, especially in the case of complexometric indicators. Xylenol Orange, for example, oxidizes slowly in aqueous solution, and the oxidation product will give a coloured complex only with copper(II). The storage life of all reagents should be checked and appropriate recommendations made for their preparation.

End-point sharpness

The accuracy of a titration will be partly determined by the volume of titrant required to traverse the end-point, and on how accurately the end-point can be located within that volume. As discussed in specialist texts and articles,[32] the equivalence point may not exactly correspond to the end-point, and a correction may be necessary. The correction may be calculated or empirical. The "sharpness index" or "relative precision"[33] may be used as a means of indicating the size of the end-point error. It is essential that *some* numerical value be given for the sharpness. If indicators are used, the volume of titrant needed to give the complete colour change must be determined and reported, and if possible the colours should be described in terms of the C.I.E. indices.[34]

Other influences

Electromagnetic radiation, usually in the form of visible or ultraviolet light, can not only affect the stability of the reactants but may also participate in the reaction or accelerate or introduce side-reactions. It is therefore sometimes necessary to perform titrations under special lighting conditions, and in indirect determinations it is often necessary to keep the reaction mixture in the dark during the reaction period before the back-titration.

Ultrasonic waves have occasionally been used to affect the course of a reaction. Pressure changes, though often used in technology, are not used in titrations, because of the experimental complications introduced.

RESULTS AND APPLICATIONS

Once the method has been worked out, it is necessary to validate it by standardization, and by application to standard samples containing the species of interest. The standardization is customarily done by preparing a standard solution of known concentration and titrating equal portions of it. In our opinion this is not a sound practice. First, all measurements are made by volume, and as discussed by Conway,[35] it is then necessary to calibrate all apparatus used, so that the personal error may be assessed. Secondly, once the first titration has been done, the tendency is to add rapidly almost the required volume of titrant to the second sample and only the last few drops are added slowly. The result is a variable drainage error, if a normal gravity-feed burette is used.[35] Furthermore, if fractions of a division are estimated in reading the burette, there is an unconscious urge to make the readings agree as closely as possible. It is much more reliable to make up the standard solution by weight and to take different weight fractions of it. Each titration must then be done more or less individually without reference to the others (unless the operator is unable to resist doing mental arithmetic), and the error in the amount of sample taken will be virtually eliminated. If a sufficiently wide range of sample weights is taken, a plot of "taken" against "found" will reveal any bias in the results, and the existence of any "blank" correction. Repetition of the procedure in the presence of the other elements expected to occur in any applications will reveal the extent of any interference by these species. The concentration ratios used must be realistic.[3]

Finally, the method must be applied to standard samples of the materials for which it is suitable, and the results compared statistically with those obtained by the best previously existing methods. It is essential to have enough replicate determinations to make the statistics meaningful, and the Snedecor F-test or "Student's" t should be applied as a criterion of significant improvement.[36]

PUBLICATION OF RESULTS

If the work has been successful, then in the preparation of a paper for publication it is necessary to report on all the features dealt with above. In particular, attention must be paid to the following points.

1. Stability of reagents, and special precautions to be taken in their preparation and storage.
2. Standardization of reagents and calibration of apparatus, with details given of the errors actually obtained.
3. Proof of the stoichiometry, and establishment of the tolerance ranges[37] for concentrations of reactants, interferents, and other species necessarily present.
4. The speed of the reaction, especially with regard to end-point detection and to the standing time in the case of indirect determinations.
5. The nature of the end-point detection, with specification of sharpness of any colour changes, details of indicator corrections or other end-point corrections. In cases of "dead-stop" methods *etc*, the response time of the indicating system should be expressed in terms of amount of titrant added, if the titrant is being added automatically or generated electrolytically. In coulometric work the current efficiency must be determined, and the timing error should be established and reported.
6. In description of the procedure, all tolerances on amounts of reagents should be clearly stated, and any special precautions stated.[37]
7. There must be adequate validation of results, supported by statistical analysis.
8. Applications of the method must be proposed and at least some of them validated experimentally. There must be a proper comparison with existing methods.
9. If possible, the method should be tested by someone who has not used it before, and *those* results quoted as well.

Résumé—On a établi les conditions nécessaires pour le développement de méthodes titrimétriques et pour la rédaction du travail pour publication. On discute des principes généraux de divers types de réaction de titrage, et l'on prête particulièrement attention aux paramètres qui influent sur les réactions chimiques.

Zusammenfassung—Die Anforderungen an die Ausarbeitung titrimetrischer Methoden und an zu publizierende Manuskripte mit solchen Themen werden aufgeführt. Die allgemeinen Grundlagen für verschiedene Typen von Titrationsreaktionen werden erörtert und dabei besonderes Gewicht auf die Parameter gelegt, die chemische Reaktionen beeinflussen.

REFERENCES

1. H. Beckurts, *Massanalyse*, Vieweg Verlag, Braunschweig, 1913.
2. G. F. Kirkbright, *Talanta*, 1966, **13**, 1.
3. L. Erdey, L. Polós and R. A. Chalmers, *ibid.*, 1970, **17**, 1143.
4. G. E. F. Lundell, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 221.
5. F. Penny, *Chem. Gaz.*, 1850, **8**, 330.
6. F. Margueritte, *Compt. Rend.*, 1846, **22**, 587.
7. *e.g.*, K. Sriraman, *Talanta*, 1971, **18**, 361.
8. R. A. Chalmers, *Aspects of Analytical Chemistry*, Oliver and Boyd, Edinburgh, 1968.
9. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1964.
10. I. M. Kolthoff, *Z. Anal. Chem.*, 1927, **70**, 395 (see also K. Fajans and O. Hassel, *Z. Electrochem.*, 1923, **29**, 495).
11. R. Belcher, A. M. G. Macdonald and E. Parry, *Anal. Chim. Acta*, 1957, **16**, 524.
12. J. Block and O. B. Waters, *Talanta*, 1967, **14**, 1130.
13. E. Wànninen, *ibid.*, 1968, **15**, 717.
14. C. R. Murty and G. G. Rao, *ibid.*, 1972, **19**, 45.
15. R. A. Chalmers and C. C. Miller, *Analyst*, 1952, **77**, 2.
16. F. Haber and J. Weiss, *Naturwissen.*, 1932, **20**, 948; *Proc. Roy. Soc.*, 1934, **A147**, 332.
17. R. A. Chalmers, D. E. Edmond and W. Moser, *Anal. Chim. Acta*, 1966, **35**, 404.
18. E. Lenssen and J. Löwenthal, *J. Prakt. Chem.*, 1862, **87**, 193.
19. A. Ringbom, *op. cit.*, p. 93.
20. W. Huber, *Titrations in Non-Aqueous Solvents*, Academic Press, New York, 1967.
21. I. Kucharský and L. Šafařík, *Titrations in Non-Aqueous Solvents*, Elsevier, London, 1965.
22. I. Gyenes, *Titration in Non-Aqueous Media*, Iliffe, London, 1967.
23. J. B. Headridge, *Photometric Titrations*, 2nd Ed., Pergamon, Oxford, 1961.
24. J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, 1954, **10**, 356.
25. H. Flaschka and S. Khalafalla, *Z. Anal. Chem.*, 1957, **156**, 401.
26. G. L. Boorman and W. B. Holbrook, *Anal. Chem.*, 1959, **31**, 10.
27. H. M. N. H. Irving and W. R. Tomlinson, *Talanta*, 1968, **15**, 1267.
28. H. Flaschka, J. Butcher and R. Speights, *ibid.*, 1961, **8**, 400.
29. J. C. Jungers, *Cinétique chimique appliquée*, Societé des Éditions Technic, Paris, 1958.
30. R. Brdička, *Grundlagen der physikalischen Chemie*, Deutscher Verlag der Wissenschaften, Berlin, 1963.
31. A. Ringbom, *op. cit.*, p. 24.
32. *e.g.*, H. A. Laitinen, *Chemical Analysis*, McGraw-Hill, New York, 1960.
    E. Bishop, in *Comprehensive Analytical Chemistry*, Vol. 1B (eds. C. L. Wilson and D. W. Wilson), Elsevier, Amsterdam, 1960.
33. A. A. Benedetti-Pichler, *Essentials of Quantitative Analysis*, Ronald Press, New York, 1956.
34. *e.g.*, S. Kotrlý and K. Vytřas, *Talanta*, 1971, **18**, 253.
35. E. J. Conway, *Micro-Diffusion Analysis and Volumetric Error*, Crosby Lockwood, London, 1947.
36. K. Eckschlager, *Errors, Measurements and Results in Chemical Analysis*, pp. 111 and 118. Van Nostrand Reinhold, London, 1969.
37. A. L. Wilson, *Talanta*, 1970, **17**, 21, 31.

Talanta, 1972, Vol. 19, pp. 761 to 768. Pergamon Press. Printed in Northern Ireland

ON THE ELECTROLYTIC ACCUMULATION OF HALIDE IONS AT HANGING MERCURY DROP ELECTRODES

A. BARAŃSKI and Z. GALUS
Institute of Fundamental Problems of Chemistry, University of Warsaw, Warsaw, Poland

(*Received* 27 *June* 1971. *Accepted* 7 *November* 1971)

Summary—The process of electrolytic accumulation of halide ions as Hg_2X_2 at the hanging mercury drop electrode is considered theoretically. The efficiency of this process is explained by considering various chemical reactions of mercury ions with halogens, and the adsorption of Hg_2X_2. The agreement of these considerations with experimental results obtained by other authors is found to be satisfactory.

ANODIC-STRIPPING VOLTAMMETRY has gained wide application[1] as a sensitive method for determination of trace metal ion impurities. The anodic stripping is preceded by electrolytic accumulation in the hanging mercury drop electrode (HMDE), of the metal to be determined. This method may also be applied with considerable success to the determination of anions[2,3] by the formation (in the accumulation step) of sparingly soluble salts of the anions with mercurous ions. However, some aspects of the anion determination are not yet clear. For instance the complex character of the dependence of electrolytic accumulation on potential, and the relatively low sensitivity in comparison to metal ion determination, have not been fully explained. These problems will be discussed in the present paper.

The anomalous dependence of the efficiency of accumulation on potential, observed in the determination of halide ions, has been explained[2] in terms of crystallization of mercurous halide at some distance from the electrode if electrolytic accumulation was achieved at very positive potentials. These microcrystals should not be adsorbed at the solution–mercury interface. The occurrence of such crystallization in very dilute solutions (10^{-5}–$10^{-6}M$) does not seem very probable. The anomalous effects may also be explained by taking into account the formation of complexes of the anions with mercury ions, and later diffusion of the complexes away from the surface of the electrode. Kemula and Taraszewska[4] have attempted to explain the sensitivity limits of the determination of halides, based on precipitate complex equilibria, but satisfactory results were obtained only for chloride.

THEORETICAL

During electrolytic accumulation of halide ions on the mercury electrode the following reactions take place:

$$2Hg + 2X^- \rightleftharpoons Hg_2X_2 + 2e \quad (1)$$

$$2Hg \rightleftharpoons Hg_2^{2+} + 2e \quad (2)$$

$$Hg + nX^- \rightleftharpoons HgX_n^{2-n} + 2e \quad (3)$$

where $n = 0, 1, 2, 3, \ldots$

Hg_2X_2 is adsorbed on the electrode, the other products of reactions (2) and (3) diffuse away. Since the activity of the halide ions increases with distance from the electrode the following interactions may occur

$$HgX_n^{2-n} + X^- \rightleftharpoons HgX_{n+1}^{1-n} \qquad (4)$$

$$Hg_2^{2+} + 2X^- \rightleftharpoons Hg_2X_2 \qquad (5)$$

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(aq) \qquad (6)$$

We have to assume that the products of these reactions are in a state of molecular distribution. This assumption is indisputable in respect to the products of (4) and (6), and should also be fulfilled in respect to reaction (5) since the concentrations of the reactants are low. Also, if $[Hg_2^{2+}] < [X^-]$ the role of reaction (5) should be small.

The equations describing the concentrations of various species existing in the solution may be obtained from Fick's second law of diffusion with the addition of kinetic terms. By taking the sum of these equations we obtain

$$\frac{\partial C_X^*(x,t)}{\partial t} = D\frac{\partial^2 C_X^*(x,t)}{\partial x^2} \qquad (7)$$

where D is the diffusion coefficient (equal for all species), and $C_X^*(x,t)$, the analytical concentration of halide, is given by

$$C_X^*(x,t) = C_X(x,t) + 2C_{Hg_2X_2}(x,t) + \sum_{n=1}^{N} nC_{HgX_n}(x,t) \qquad (8)$$

By consideration of mass balance we obtain

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}D\left(\frac{\partial C_X^*}{\partial x}\right)_{x=0} \qquad (9)$$

where $\Gamma_{Hg_2X_2}$ denotes the surface concentration of the accumulated species. Using the solutions to equation (7) we may write (*a*) for a plane electrode in quiet solutions

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}\frac{D^{1/2}}{(\pi t)^{1/2}}[C_X^0 - C_X^*(x=0)] \qquad (10)$$

and (*b*) for accumulation with uniform mixing of the solution

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}\frac{D}{\delta}[C_X^0 - C_X^*(x=0)] \qquad (11)$$

where C_X^0 and C_X^* $(x = 0)$ denote the analytical concentrations of X^- in the bulk of the solution and at the surface of the electrode respectively, and δ is the thickness of the diffusion layer.

The function $\varphi = [C_X^0 - C_X^*(x=0)]/C_X^0$ (the coefficient of efficiency of electrolytic accumulation) is also introduced. This function may be calculated on the assumption that all processes occurring at the surface of the electrode are reversible. Then the concentrations of all species at the electrode surface may be calculated from the following equilibria

$$[Hg_2^{2+}] = \exp\frac{2F}{RT}(E - E^0) \qquad (12)$$

$$[Hg^{2+}] = K[Hg_2^{2+}] \qquad (13)$$

$$[Hg_2^{2+}][X^-]^2 = K_{s0}f(\theta) \qquad (14)$$

$$[HgX_n^{2-n}] = \beta n[Hg^{2+}][X^-]^n \qquad (15)$$

$$[Hg_2X_2]_b \sim 0 \qquad (16)$$

where E^0 is the standard potential of the Hg_2^{2+}/Hg couple, K_{s0} the solubility product of Hg_2X_2, β_n the stability constants of the halide complexes, and $[Hg_2X_2]_b$ the bulk concentration of Hg_2X_2.

From these arguments we obtain

$$\varphi = 1 - \frac{1}{C_X^0}\left\{\sqrt{K_{s0}f(\theta)}\exp\left[\frac{-F(E-E^0)}{RT}\right] + \sum_{n=1}^{N} n\beta_n K\,[K_{s0}f(\theta)]^{n/2}\exp\left[\frac{(2-n)F(E-E^0)}{RT}\right]\right\} \qquad (17)$$

In these equations $f(\theta)$ denotes the activity of Hg_2X_2 on the surface of the electrode, as a function of the degree of coverage θ ($\theta = \Gamma/\Gamma_m$). Alternatively, $f(\theta)$ may be formulated in terms of the dependence of the equilibrium adsorption $\Gamma_{Hg_2X_2}$ on $[Hg_2X_2]_b$ where

$$[Hg_2X_2]_b = \beta_2{}^*[Hg_2^{2+}][X^-]^2 \qquad (18)$$

If for $\theta < 1$ we assume that the Langmuir isotherm is obeyed, then

$$[Hg_2X_2]_b = \frac{\beta\theta}{1-\theta} \qquad (19)$$

and

$$[Hg_2^{2+}][X^-]^2 = \frac{\beta\theta}{\beta_2{}^*(1-\theta)} \qquad (20)$$

From (14) and (20) we obtain

$$f(\theta) = \frac{\beta\theta}{K_{s2}(1-\theta)} \qquad (21)$$

where β is the equilibrium adsorption constant and $K_{s2} = \beta_2{}^*K_{s0}$. When $[Hg_2X_2]$ reaches the K_{s2} value, crystallization begins, $\theta > 1$ and multilayers form on the surface of the electrode.

Then

$$[Hg_2^{2+}][X^-]^2 = \frac{K_{s2}}{\beta_2{}^*} = K_{s0}$$

and

$$f(\theta) = 1$$

It is not useful to apply equation (21) together with (17) in these considerations, because the value of $\beta_2{}^*$ is not known. Furthermore, additional experiments should be carried out to find whether the Langmuir adsorption is obeyed. The potential dependence of the adsorption constant should also be determined. It will not be possible then, to calculate precisely the efficiency of the electrolytic accumulation; however, some other interesting parameters of the accumulation process may be predicted. The value of $f(\theta)$ may be determined only by experimentation; its determination will be difficult, however, even if it is possible.

Since in systems with halide concentrations lower then $10^{-4}M$ only the complexes HgX and HgX_2 are present, equation (17) may be simplified to

$$\varphi = 1 - \frac{2}{C_X^0}\left\{\beta_2KK_{s0}f(\theta) + \sqrt{\beta_1KK_{s0}f(\theta)}\cosh\left[\frac{F(E-E_{max})}{RT}\right]\right\} \qquad (22)$$

where

$$E_{\max} = E^0 - \frac{RT}{2F} \ln \beta_1 K$$

If $f(\theta)$ and the constants in (22) are assumed to be independent of the potential then $E_{\max}$ determines the potential of the maximum efficiency of electrolytic accumulation. In Fig. 1 the dependence of φ on E for Cl^-, Br^- and I^- is given, calculated with the use of equation (22), assuming $f(\theta) = 1$ and $C_X{}^0 = 10^{-5}M$.

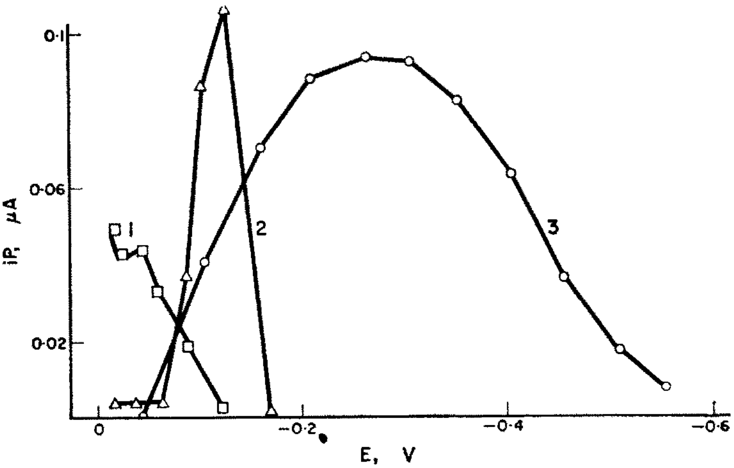


FIG. 1.—The dependence of the coefficient of efficiency of electrolytic accumulation on the accumulation potential, calculated according to equation (22) for Cl^- (curve 1), Br^- (2), and I^- (3).

The following values were used in the calculation:

$f(\theta) = 1$, $C_X{}^0 = 10^{-5}M$, $\log K = -1{\cdot}94$[5];
$\log \beta_1 = 6{\cdot}74$, $\log \beta_2 = 13{\cdot}22$, $\log K_{s0} = -16{\cdot}88$ for Cl^- [5];
$\log \beta_1 = 9{\cdot}02$, $\log \beta_2 = 17{\cdot}30$, $\log K_{s0} = -21{\cdot}28$ for Br^- [6];
$\log \beta_1 = 12{\cdot}87$, $\log \beta_2 = 23{\cdot}79$, $\log K_{s0} = -27{\cdot}46$ for I^-.[7]
Potentials are given with respect to the $Hg/Hg_2SO_4/1M\ H_2SO_4$ electrode.

An important relationship, from the analytical point of view, between time of electrolytic accumulation and $\Gamma_{Hg_2X_2}$ may be formulated on the basis of equations (10), (11) and (22). It is scarcely possible to give a strict time dependence if the function $f(\theta)$ is not precisely defined; however, the asymptotic solutions may be obtained for times that are short or long in comparison to the time needed to obtain full coverage of the electrode by a monolayer.

1. Short accumulation times.

When $t \to 0$ then $\theta \to 0$, $f(\theta) \to 0$ and $\varphi \to 1$.

If the accumulation is carried out in quiet solutions then

$$\Gamma_{Hg_2X_2} = \sqrt{\frac{Dt}{\pi}}\, C_X{}^0 \tag{23}$$

and for stirred solutions,

$$\Gamma_{Hg_2X_2} = \frac{D}{2\delta}\, C_X{}^0 t \tag{24}$$

2. Long accumulation times.

Two cases may be distinguished, in dependence on $C_X{}^0$.

When

$$C_X{}^0 > L_1(E)$$

where

$$L_1(E) = 2\left\{\beta_2 KK_{s0} + \sqrt{\beta_1 KK_{s0}}\cosh\left[\frac{F(E - E_{\max})}{RT}\right]\right\}$$

and $t \rightarrow \infty$, then $f(\theta) = 1$, $\varphi = \text{const.}$

For solutions not stirred during electrolytic accumulation we have

$$\Gamma_{Hg_2X_2} = C_1 + \sqrt{\frac{Dt}{\pi}}\,\varphi C_X{}^0 \tag{25}$$

For stirred solutions

$$\Gamma_{Hg_2X_2} = C_2 + \frac{DC_X{}^0}{2\delta}\,\varphi t \tag{26}$$

where C_1 and C_2 are constants equal to or larger then 0.

Equations (25) and (26) are valid as long as the transport of ions from the bulk of the solution is slower then the rate of the transport through the layer covering the electrode surface.

In the second case

$$C_X{}^0 < L_1(E)$$

and the coefficient of efficiency of electrolytic accumulation will assume positive values only for $f(\theta) < 1$. This means that θ cannot be larger then $\theta_{\max}$, which itself is independent of the mode of electrolytic accumulation. The function $f(\theta_{\max})$ may be defined from equation (22).

When $t \rightarrow \infty$, then $\varphi \rightarrow 0$ and

$$f(\theta_{\max}) = \frac{C_X{}^0}{2\beta_2 KK_{s0}}\left[\sqrt{\frac{L_2(E)}{C_X{}^0}} + 1 - \sqrt{\frac{L_2(E)}{C_X{}^0}}\right]^2 \tag{27}$$

where

$$L_2(E) = \frac{\beta_1}{2\beta_2}\cosh^2\left[\frac{F(E - E_{\max})}{RT}\right] \tag{28}$$

In Fig. 2a the dependence of $f(\theta_{\max})$ on E, calculated with the use of equation (27), is given for $10^{-6}M$ Cl^-, Br^-, I^-. In Fig. 3 the dependence of $\Gamma_{Hg_2X_2}$ on t is shown for various concentration ranges and electrolytic accumulation with uniform stirring of the solution.

Comparison of theory with experiment

The experimental dependence of peak current (i_p) of accumulated Hg_2X_2 on the deposition potential, found by Kemula, Kublik and Taraszewska[2] in their chronovoltammetric determination of halide ions with the use of the HMDE is given in Fig. 2b. A similar dependence was found by Perchard, Buvet and Molina.[3] The equations (22) and (27) explain these experiments semi-quantitatively. A strict quantitative correlation between φ or $f(\theta_{\max})$ and i_p calls for experimental determination of $f(\theta)$ and $i_p(\theta)$. One may suppose that for low coverages both dependences are linear; this may, however, be confirmed only by experiment.

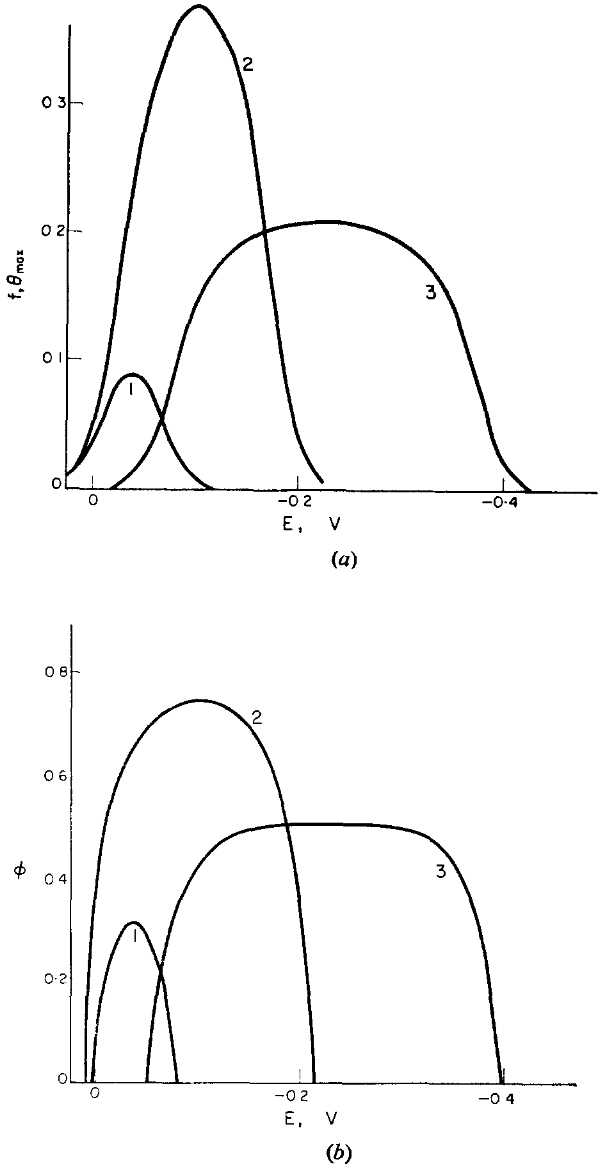


FIG. 2.—(*a*) The dependence of $f(\theta_{max})$ on the accumulation potential, calculated according to equation (27) for Cl^- (curve 1), Br^-(2) and I^-(3).

The values of equilibrium constants were taken from the literature[5–8] and $C_X{}^0$ was assumed to be $10^{-6}M$. The potential is given with respect to the $Hg/Hg_2SO_4/1M$ H_2SO_4 electrode

(*b*) Experimental dependence of peak current on the accumulation potential[2] for determination of $10^{-5}M$ Cl^- (curve 1), $10^{-6}M$ Br^-(2); $10^{-6}M$ I^-(3). In experiments with the HMDE, 0·01*N* H_2SO_4 served as background electrolyte, and the accumulation time was 120 sec.

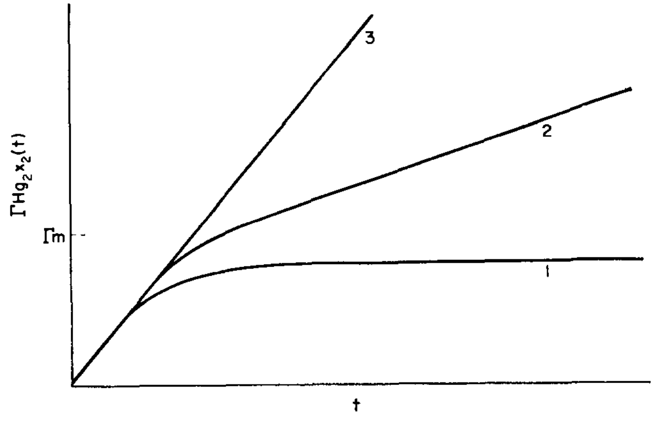


FIG 3.—Dependence of $\Gamma_{Hg_2X_2}$ on t, obtained with use of equations (24), (26) and (27). Curve 1 for $C_X{}^0 < L_1(E)$, curve 2 for $C_X{}^0 > L_1(E)$ and curve 3 for $C_X{}^0 \gg L_1(E)$.

A satisfactory agreement was found between the theoretical and experimental potentials for maximum efficiency of the electrolytic accumulation (Table I). Experimental values of E_{max} were taken from figures given in both the cited papers.

The small differences in E_{max} may be due to different concentrations of background electrolytes and their influence on the adsorption equilibrium constant. The specific adsorption of $SO_4{}^{2-}$ and $ClO_4{}^-$ ions and their interaction with Hg_2X_2 in the adsorbed state may also be responsible for these differences.

TABLE I.—EXPERIMENTAL AND THEORETICAL POTENTIAL E_{max}

Ion	E_{max} theoretical, mV	E_{max} experimental, mV	
		Ref. 2*	Ref. 3†
Cl^-	−37	−45	−87
Br^-	−105	−127	−82
I^-	−222	−258	−232

* Composition of the solutions: Cl^- $10^{-5}M$; Br^- $10^{-6}M$; I^- $10^{-6}M$; all in $0{\cdot}01N$ H_2SO_4

† Composition of the solutions: Cl^- $5 \times 10^{-4}M$; Br^- $5 \times 10^{-5}M$; I^- $5 \times 10^{-6}M$; all in $0{\cdot}1M$ $HClO_4$.

The theoretical dependence of $\Gamma_{Hg_2X_2}$ on t may be compared with experiments carried out to establish the dependence of i_p on the time of electrolytic accumulation. The assumption that the peak current is linearly dependent on $\Gamma_{Hg_2X_2}$ has to be made. Such a linear dependence was found by Perchard *et al.*[3] in their study of deposition of chlorides from $5 \times 10^{-5}M$ solution. This dependence corresponds to curve 3 in Fig. 3. The magnitude of the measured peak currents indicates multilayer coverage.

The same authors, in their determination of Cl^-, Br^- and I^- at concentrations not exceeding $10^{-5}M$ found a linear i_p–t relationship only for short accumulation times. With longer times the peak current was independent of the time of deposition, as is illustrated by curve 1 in Fig. 3. In this case the peak current shows that the electrode coverage at its maximum is a monolayer. Such a dependence was found also by Kemula, Kublik and Taraszewska.[2]

The limiting experimental value of concentration, $10^{-5}M$, agrees with the theoretical value of $L_1(E_{\max})$ which is $7 \cdot 3 \times 10^{-6}$, $1 \cdot 3 \times 10^{-6}$ and $4 \cdot 4 \times 10^{-6}M$ for Cl^-, Br^- and I^- respectively.

The considerations presented do not give a complete and precise picture of the process of electrolytic accumulation of halogen ions at mercury electrodes, since they are limited to dealing with the transport phenomena. The full knowledge of this process, especially at low coverages, calls for the determination of the mode of adsorption. We intend to study this problem in the near future.

The arguments given refer to halide ions, but similar reasoning may be applied to other systems.

Zusammenfassung—Die elektrolytische Anreicherung von Halogenidionen als Hg_2X_2 am hängenden Quecksilbertropfen wird theoretisch erörtert. Zur Erklärung werden verschiedene chemische Reaktionen von Quecksilberionen mit Halogenen in Betracht gezogen sowie die Adsorption von Hg_2X_2. Die Übereinstimmung mit den Versuchsergebnissen anderer Autoren ist zufriedenstellend.

Résumé—On considére thèoriquement le processus d'accumulation èlectrolytique d'ions halogènures à l'ètat Hg_2X_2 sur l'èlectrode à goutte de mercure pendante. L'efficacité de ce processus est expliquée en considérant diverses réactions chimiques d'ions mercure avec les halogènes, et l'adsorption de Hg_2X_2. On a trouvé satisfaisant l'accord de ces considérations avec les résultats expérimentaux obtenus par d'autres auteurs.

REFERENCES

1. W. Kemula and Z. Kublik, *Advan. Anal. Chem. Instr.*, 1963, **2**, 123; R. Neeb, *Inverse Polarographie und Voltammetrie. Neuere Verfahren zur Spurenanalyse*, Akademie Verlag, Berlin, 1969.
2. W. Kemula, Z. Kublik and J. Taraszewska, *Microchem. J. Symp.* 1962, **1**, 865.
3. J. P. Perchard, M. Buvet and R. Molina, *J. Electroanal. Chem.*, 1967, **14**, 57.
4. W. Kemula and J. Taraszewska, *Rev. Chim. Minerale*, 1968, **5**, 535.
5. S. Hietanen and L. G. Sillén, *Arkiv Kemi*, 1956, **10**, 103.
6. B. Lindgren, A. Jonsson and L. G. Sillén, *Acta Chem. Scand.*, 1947, **1**, 479.
7. P. O. Bethge, I. Jonevall-Westöö and L. G. Sillén, *ibid.*, 1948, **2**, 828.
8. I. Qvarfort and L. G. Sillén, *ibid.*, 1949, **3**, 505.

Talanta, 1972, Vol. 19, pp. 761 to 768. Pergamon Press. Printed in Northern Ireland

ON THE ELECTROLYTIC ACCUMULATION OF HALIDE IONS AT HANGING MERCURY DROP ELECTRODES

A. Barański and Z. Galus
Institute of Fundamental Problems of Chemistry, University of Warsaw, Warsaw, Poland

(*Received* 27 *June* 1971. *Accepted* 7 *November* 1971)

Summary—The process of electrolytic accumulation of halide ions as Hg_2X_2 at the hanging mercury drop electrode is considered theoretically. The efficiency of this process is explained by considering various chemical reactions of mercury ions with halogens, and the adsorption of Hg_2X_2. The agreement of these considerations with experimental results obtained by other authors is found to be satisfactory.

Anodic-stripping voltammetry has gained wide application[1] as a sensitive method for determination of trace metal ion impurities. The anodic stripping is preceded by electrolytic accumulation in the hanging mercury drop electrode (HMDE), of the metal to be determined. This method may also be applied with considerable success to the determination of anions[2,3] by the formation (in the accumulation step) of sparingly soluble salts of the anions with mercurous ions. However, some aspects of the anion determination are not yet clear. For instance the complex character of the dependence of electrolytic accumulation on potential, and the relatively low sensitivity in comparison to metal ion determination, have not been fully explained. These problems will be discussed in the present paper.

The anomalous dependence of the efficiency of accumulation on potential, observed in the determination of halide ions, has been explained[2] in terms of crystallization of mercurous halide at some distance from the electrode if electrolytic accumulation was achieved at very positive potentials. These microcrystals should not be adsorbed at the solution–mercury interface. The occurrence of such crystallization in very dilute solutions (10^{-5}–$10^{-6}M$) does not seem very probable. The anomalous effects may also be explained by taking into account the formation of complexes of the anions with mercury ions, and later diffusion of the complexes away from the surface of the electrode. Kemula and Taraszewska[4] have attempted to explain the sensitivity limits of the determination of halides, based on precipitate complex equilibria, but satisfactory results were obtained only for chloride.

THEORETICAL

During electrolytic accumulation of halide ions on the mercury electrode the following reactions take place:

$$2Hg + 2X^- \rightleftharpoons Hg_2X_2 + 2e \tag{1}$$

$$2Hg \rightleftharpoons Hg_2^{2+} + 2e \tag{2}$$

$$Hg + nX^- \rightleftharpoons HgX_n^{2-n} + 2e \tag{3}$$

where $n = 0, 1, 2, 3, \ldots$

Hg_2X_2 is adsorbed on the electrode, the other products of reactions (2) and (3) diffuse away. Since the activity of the halide ions increases with distance from the electrode the following interactions may occur

$$HgX_n^{2-n} + X^- \rightleftharpoons HgX_{n+1}^{1-n} \tag{4}$$

$$Hg_2^{2+} + 2X^- \rightleftharpoons Hg_2X_2 \tag{5}$$

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(aq) \tag{6}$$

We have to assume that the products of these reactions are in a state of molecular distribution. This assumption is indisputable in respect to the products of (4) and (6), and should also be fulfilled in respect to reaction (5) since the concentrations of the reactants are low. Also, if $[Hg_2^{2+}] < [X^-]$ the role of reaction (5) should be small.

The equations describing the concentrations of various species existing in the solution may be obtained from Fick's second law of diffusion with the addition of kinetic terms. By taking the sum of these equations we obtain

$$\frac{\partial C_X^*(x, t)}{\partial t} = D\frac{\partial^2 C_X^*(x, t)}{\partial x^2} \tag{7}$$

where D is the diffusion coefficient (equal for all species), and $C_X^*(x, t)$, the analytical concentration of halide, is given by

$$C_X^*(x, t) = C_X(x, t) + 2C_{Hg_2X_2}(x, t) + \sum_{n=1}^{N} nC_{HgX_n}(x, t) \tag{8}$$

By consideration of mass balance we obtain

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}D\left(\frac{\partial C_X^*}{\partial x}\right)_{x=0} \tag{9}$$

where $\Gamma_{Hg_2X_2}$ denotes the surface concentration of the accumulated species. Using the solutions to equation (7) we may write (*a*) for a plane electrode in quiet solutions

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}\frac{D^{1/2}}{(\pi t)^{1/2}}[C_X^0 - C_X^* (x = 0)] \tag{10}$$

and (*b*) for accumulation with uniform mixing of the solution

$$\frac{d\Gamma_{Hg_2X_2}}{dt} = \frac{1}{2}\frac{D}{\delta}[C_X^0 - C_X^* (x = 0)] \tag{11}$$

where C_X^0 and C_X^* $(x = 0)$ denote the analytical concentrations of X^- in the bulk of the solution and at the surface of the electrode respectively, and δ is the thickness of the diffusion layer.

The function $\varphi = [C_X^0 - C_X^* (x = 0)]/C_X^0$ (the coefficient of efficiency of electrolytic accumulation) is also introduced. This function may be calculated on the assumption that all processes occurring at the surface of the electrode are reversible. Then the concentrations of all species at the electrode surface may be calculated from the following equilibria

$$[Hg_2^{2+}] = \exp\frac{2F}{RT}(E - E^0) \tag{12}$$

$$[Hg^{2+}] = K[Hg_2^{2+}] \tag{13}$$

$$[Hg_2^{2+}][X^-]^2 = K_{s0}f(\theta) \tag{14}$$

$$[HgX_n^{2-n}] = \beta n[Hg^{2+}][X^-]^n \tag{15}$$

$$[Hg_2X_2]_b \sim 0 \tag{16}$$

where E^0 is the standard potential of the Hg_2^{2+}/Hg couple, K_{s0} the solubility product of Hg_2X_2, β_n the stability constants of the halide complexes, and $[Hg_2X_2]_b$ the bulk concentration of Hg_2X_2.

From these arguments we obtain

$$\varphi = 1 - \frac{1}{C_X{}^0}\left\{\sqrt{K_{s0}f(\theta)}\exp\left[\frac{-F(E-E^0)}{RT}\right] + \sum_{n=1}^{N} n\beta_n K\,[K_{s0}f(\theta)]^{n/2}\exp\left[\frac{(2-n)F(E-E^0)}{RT}\right]\right\} \qquad (17)$$

In these equations $f(\theta)$ denotes the activity of Hg_2X_2 on the surface of the electrode, as a function of the degree of coverage θ ($\theta = \Gamma/\Gamma_m$). Alternatively, $f(\theta)$ may be formulated in terms of the dependence of the equilibrium adsorption $\Gamma_{Hg_2X_2}$ on $[Hg_2X_2]_b$ where

$$[Hg_2X_2]_b = \beta_2{}^*[Hg_2{}^{2+}][X^-]^2 \qquad (18)$$

If for $\theta < 1$ we assume that the Langmuir isotherm is obeyed, then

$$[Hg_2X_2]_b = \frac{\beta\theta}{1-\theta} \qquad (19)$$

and

$$[Hg_2{}^{2+}][X^-]^2 = \frac{\beta\theta}{\beta_2{}^*(1-\theta)} \qquad (20)$$

From (14) and (20) we obtain

$$f(\theta) = \frac{\beta\theta}{K_{s2}(1-\theta)} \qquad (21)$$

where β is the equilibrium adsorption constant and $K_{s2} = \beta_2{}^*K_{s0}$. When $[Hg_2X_2]$ reaches the K_{s2} value, crystallization begins, $\theta > 1$ and multilayers form on the surface of the electrode.

Then

$$[Hg_2{}^{2+}][X^-]^2 = \frac{K_{s2}}{\beta_2{}^*} = K_{s0}$$

and

$$f(\theta) = 1$$

It is not useful to apply equation (21) together with (17) in these considerations, because the value of $\beta_2{}^*$ is not known. Furthermore, additional experiments should be carried out to find whether the Langmuir adsorption is obeyed. The potential dependence of the adsorption constant should also be determined. It will not be possible then, to calculate precisely the efficiency of the electrolytic accumulation; however, some other interesting parameters of the accumulation process may be predicted. The value of $f(\theta)$ may be determined only by experimentation; its determination will be difficult, however, even if it is possible.

Since in systems with halide concentrations lower then $10^{-4}M$ only the complexes HgX and HgX_2 are present, equation (17) may be simplified to

$$\varphi = 1 - \frac{2}{C_X{}^0}\left\{\beta_2KK_{s0}f(\theta) + \sqrt{\beta_1KK_{s0}f(\theta)}\cosh\left[\frac{F(E-E_{max})}{RT}\right]\right\} \qquad (22)$$

where

$$E_{\max} = E^0 - \frac{RT}{2F} \ln \beta_1 K$$

If $f(\theta)$ and the constants in (22) are assumed to be independent of the potential then $E_{\max}$ determines the potential of the maximum efficiency of electrolytic accumulation. In Fig. 1 the dependence of φ on E for Cl^-, Br^- and I^- is given, calculated with the use of equation (22), assuming $f(\theta) = 1$ and $C_X{}^0 = 10^{-5}M$.

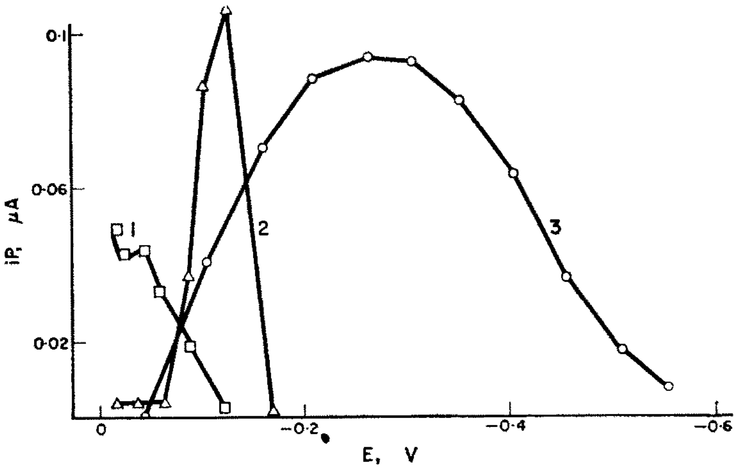


Fig. 1.—The dependence of the coefficient of efficiency of electrolytic accumulation on the accumulation potential, calculated according to equation (22) for Cl^- (curve 1), Br^- (2), and I^- (3).

The following values were used in the calculation:

$f(\theta) = 1$, $C_X{}^0 = 10^{-5}M$, $\log K = -1{\cdot}94$[5];
$\log \beta_1 = 6{\cdot}74$, $\log \beta_2 = 13{\cdot}22$, $\log K_{s0} = -16{\cdot}88$ for Cl^- [5];
$\log \beta_1 = 9{\cdot}02$, $\log \beta_2 = 17{\cdot}30$, $\log K_{s0} = -21{\cdot}28$ for Br^- [6];
$\log \beta_1 = 12{\cdot}87$, $\log \beta_2 = 23{\cdot}79$, $\log K_{s0} = -27{\cdot}46$ for I^-.[7]
Potentials are given with respect to the $Hg/Hg_2SO_4/1M\ H_2SO_4$ electrode.

An important relationship, from the analytical point of view, between time of electrolytic accumulation and $\Gamma_{Hg_2X_2}$ may be formulated on the basis of equations (10), (11) and (22). It is scarcely possible to give a strict time dependence if the function $f(\theta)$ is not precisely defined; however, the asymptotic solutions may be obtained for times that are short or long in comparison to the time needed to obtain full coverage of the electrode by a monolayer.

1. Short accumulation times.

When $t \rightarrow 0$ then $\theta \rightarrow 0$, $f(\theta) \rightarrow 0$ and $\varphi \rightarrow 1$.

If the accumulation is carried out in quiet solutions then

$$\Gamma_{Hg_2X_2} = \sqrt{\frac{Dt}{\pi}}\, C_X{}^0 \tag{23}$$

and for stirred solutions,

$$\Gamma_{Hg_2X_2} = \frac{D}{2\delta}\, C_X{}^0 t \tag{24}$$

2. Long accumulation times.

Two cases may be distinguished, in dependence on $C_X{}^0$.

When

$$C_X{}^0 > L_1(E)$$

where

$$L_1(E) = 2\left\{\beta_2 KK_{s0} + \sqrt{\beta_1 KK_{s0}}\cosh\left[\frac{F(E - E_{\max})}{RT}\right]\right\}$$

and $t \to \infty$, then $f(\theta) = 1$, $\varphi = \text{const.}$

For solutions not stirred during electrolytic accumulation we have

$$\Gamma_{Hg_2X_2} = C_1 + \sqrt{\frac{Dt}{\pi}}\,\varphi C_X{}^0 \tag{25}$$

For stirred solutions

$$\Gamma_{Hg_2X_2} = C_2 + \frac{DC_X{}^0}{2\delta}\,\varphi t \tag{26}$$

where C_1 and C_2 are constants equal to or larger then 0.

Equations (25) and (26) are valid as long as the transport of ions from the bulk of the solution is slower then the rate of the transport through the layer covering the electrode surface.

In the second case

$$C_X{}^0 < L_1(E)$$

and the coefficient of efficiency of electrolytic accumulation will assume positive values only for $f(\theta) < 1$. This means that θ cannot be larger then $\theta_{\max}$, which itself is independent of the mode of electrolytic accumulation. The function $f(\theta_{\max})$ may be defined from equation (22).

When $t \to \infty$, then $\varphi \to 0$ and

$$f(\theta_{\max}) = \frac{C_X{}^0}{2\beta_2 KK_{s0}}\left[\sqrt{\frac{L_2(E)}{C_X{}^0}} + 1 - \sqrt{\frac{L_2(E)}{C_X{}^0}}\right]^2 \tag{27}$$

where

$$L_2(E) = \frac{\beta_1}{2\beta_2}\cosh^2\left[\frac{F(E - E_{\max})}{RT}\right] \tag{28}$$

In Fig. 2a the dependence of $f(\theta_{\max})$ on E, calculated with the use of equation (27), is given for $10^{-6}M$ Cl^-, Br^-, I^-. In Fig. 3 the dependence of $\Gamma_{Hg_2X_2}$ on t is shown for various concentration ranges and electrolytic accumulation with uniform stirring of the solution.

Comparison of theory with experiment

The experimental dependence of peak current (i_p) of accumulated Hg_2X_2 on the deposition potential, found by Kemula, Kublik and Taraszewska[2] in their chronovoltammetric determination of halide ions with the use of the HMDE is given in Fig. 2b. A similar dependence was found by Perchard, Buvet and Molina.[3] The equations (22) and (27) explain these experiments semi-quantitatively. A strict quantitative correlation between φ or $f(\theta_{\max})$ and i_p calls for experimental determination of $f(\theta)$ and $i_p(\theta)$. One may suppose that for low coverages both dependences are linear; this may, however, be confirmed only by experiment.

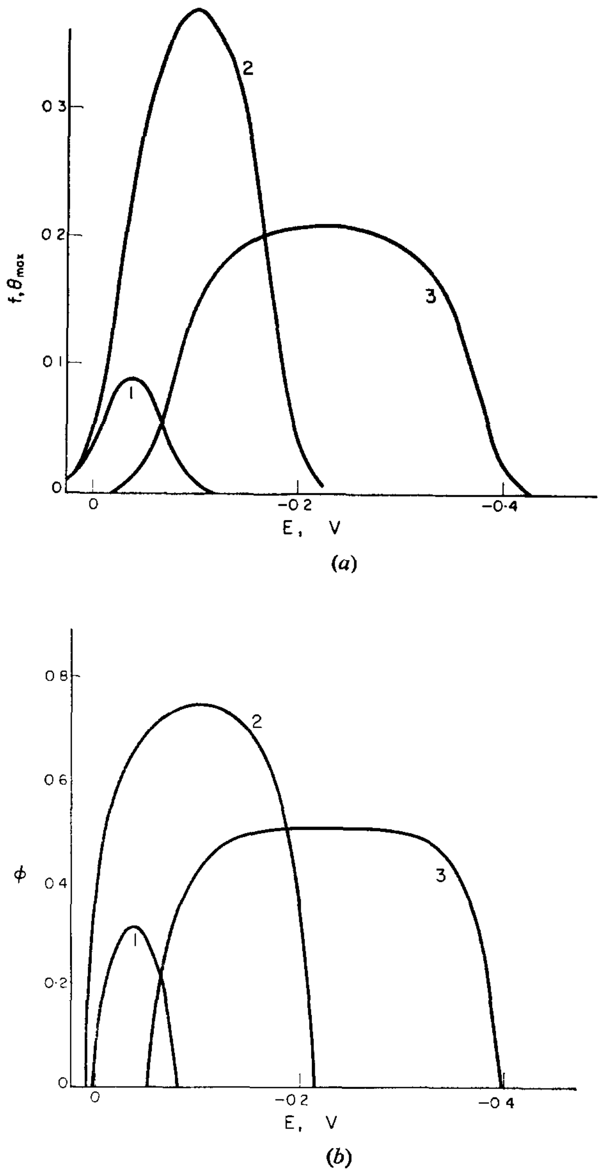


FIG. 2.—(*a*) The dependence of $f(\theta_{max})$ on the accumulation potential, calculated according to equation (27) for Cl^- (curve 1), Br^-(2) and I^-(3).

The values of equilibrium constants were taken from the literature[5–8] and $C_X{}^0$ was assumed to be $10^{-6}M$. The potential is given with respect to the $Hg/Hg_2SO_4/1M$ H_2SO_4 electrode

(*b*) Experimental dependence of peak current on the accumulation potential[2] for determination of $10^{-5}M$ Cl^- (curve 1), $10^{-6}M$ Br^-(2); $10^{-6}M$ I^-(3). In experiments with the HMDE, 0·01N H_2SO_4 served as background electrolyte, and the accumulation time was 120 sec.

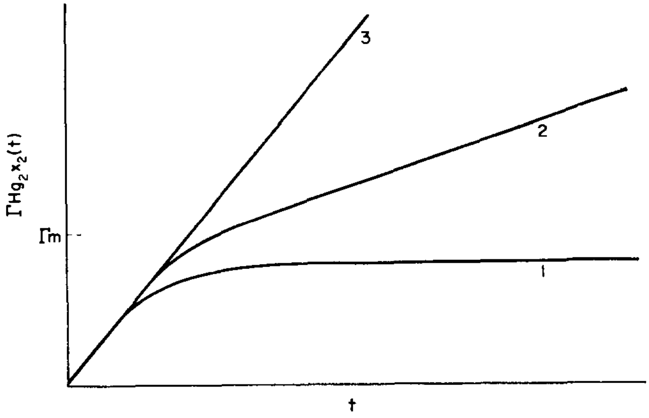


FIG 3.—Dependence of $\Gamma_{Hg_2X_2}$ on t, obtained with use of equations (24), (26) and (27). Curve 1 for $C_X{}^0 < L_1(E)$, curve 2 for $C_X{}^0 > L_1(E)$ and curve 3 for $C_X{}^0 \gg L_1(E)$.

A satisfactory agreement was found between the theoretical and experimental potentials for maximum efficiency of the electrolytic accumulation (Table I). Experimental values of E_{max} were taken from figures given in both the cited papers.

The small differences in E_{max} may be due to different concentrations of background electrolytes and their influence on the adsorption equilibrium constant. The specific adsorption of $SO_4{}^{2-}$ and $ClO_4{}^-$ ions and their interaction with Hg_2X_2 in the adsorbed state may also be responsible for these differences.

TABLE I.—EXPERIMENTAL AND THEORETICAL POTENTIAL E_{max}

Ion	E_{max} theoretical, mV	E_{max} experimental, mV	
		Ref. 2*	Ref. 3†
Cl^-	−37	−45	−87
Br^-	−105	−127	−82
I^-	−222	−258	−232

* Composition of the solutions: Cl^- $10^{-5}M$; Br^- $10^{-6}M$; I^- $10^{-6}M$; all in $0{\cdot}01N$ H_2SO_4

† Composition of the solutions: Cl^- $5 \times 10^{-4}M$; Br^- $5 \times 10^{-5}M$; I^- $5 \times 10^{-5}M$; all in $0{\cdot}1M$ $HClO_4$.

The theoretical dependence of $\Gamma_{Hg_2X_2}$ on t may be compared with experiments carried out to establish the dependence of i_p on the time of electrolytic accumulation. The assumption that the peak current is linearly dependent on $\Gamma_{Hg_2X_2}$ has to be made. Such a linear dependence was found by Perchard *et al.*[3] in their study of deposition of chlorides from $5 \times 10^{-5}M$ solution. This dependence corresponds to curve 3 in Fig. 3. The magnitude of the measured peak currents indicates multilayer coverage.

The same authors, in their determination of Cl^-, Br^- and I^- at concentrations not exceeding $10^{-5}M$ found a linear i_p–t relationship only for short accumulation times. With longer times the peak current was independent of the time of deposition, as is illustrated by curve 1 in Fig. 3. In this case the peak current shows that the electrode coverage at its maximum is a monolayer. Such a dependence was found also by Kemula, Kublik and Taraszewska.[2]

The limiting experimental value of concentration, $10^{-5}M$, agrees with the theoretical value of $L_1(E_{max})$ which is $7{\cdot}3 \times 10^{-6}$, $1{\cdot}3 \times 10^{-6}$ and $4{\cdot}4 \times 10^{-6}M$ for Cl^-, Br^- and I^- respectively.

The considerations presented do not give a complete and precise picture of the process of electrolytic accumulation of halogen ions at mercury electrodes, since they are limited to dealing with the transport phenomena. The full knowledge of this process, especially at low coverages, calls for the determination of the mode of adsorption. We intend to study this problem in the near future.

The arguments given refer to halide ions, but similar reasoning may be applied to other systems.

Zusammenfassung—Die elektrolytische Anreicherung von Halogenidionen als Hg_2X_2 am hängenden Quecksilbertropfen wird theoretisch erörtert. Zur Erklärung werden verschiedene chemische Reaktionen von Quecksilberionen mit Halogenen in Betracht gezogen sowie die Adsorption von Hg_2X_2. Die Übereinstimmung mit den Versuchsergebnissen anderer Autoren ist zufriedenstellend.

Résumé—On considère thèoriquement le processus d'accumulation èlectrolytique d'ions halogènures à l'ètat Hg_2X_2 sur l'èlectrode à goutte de mercure pendante. L'efficacité de ce processus est expliquée en considérant diverses réactions chimiques d'ions mercure avec les halogènes, et l'adsorption de Hg_2X_2. On a trouvé satisfaisant l'accord de ces considérations avec les résultats expérimentaux obtenus par d'autres auteurs.

REFERENCES

1. W. Kemula and Z. Kublik, *Advan. Anal. Chem. Instr.*, 1963, **2**, 123; R. Neeb, *Inverse Polarographie und Voltammetrie. Neuere Verfahren zur Spurenanalyse*, Akademie Verlag, Berlin, 1969.
2. W. Kemula, Z. Kublik and J. Taraszewska, *Microchem. J. Symp.* 1962, **1**, 865.
3. J. P. Perchard, M. Buvet and R. Molina, *J. Electroanal. Chem.*, 1967, **14**, 57.
4. W. Kemula and J. Taraszewska, *Rev. Chim. Minerale*, 1968, **5**, 535.
5. S. Hietanen and L. G. Sillén, *Arkiv Kemi*, 1956, **10**, 103.
6. B. Lindgren, A. Jonsson and L. G. Sillén, *Acta Chem. Scand.*, 1947, **1**, 479.
7. P. O. Bethge, I. Jonevall-Westöö and L. G. Sillén, *ibid.*, 1948, **2**, 828.
8. I. Qvarfort and L. G. Sillén, *ibid.*, 1949, **3**, 505.

Talanta, 1972, Vol. 19, pp. 769 to 787. Pergamon Press. Printed in Northern Ireland

ELECTROCHEMICAL DETERMINATION OF ADENINE AND ADENOSINE

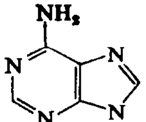
ADSORPTION OF ADENINE AND ADENOSINE AT THE PYROLYTIC GRAPHITE ELECTRODE

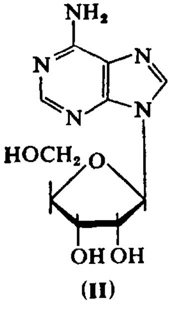
GLENN DRYHURST
Department of Chemistry, University of Oklahoma, Norman, Oklahoma, 73069, U.S.A.

(*Received* 12 *July* 1971. *Accepted* 30 *October* 1971)

Summary—Adenine and adenosine are polarographically reducible from aqueous solution at pH 4·7 at the DME at the same $E_{1/2}$, and are also voltammetrically oxidizable at the PGE, but at different potentials, adenosine at higher potentials. Competitive adsorption of both compounds at the PGE results in a decrease in the scanning voltammetric oxidation peak of adenine in the presence of adenosine, reaching a constant value when the concentration of the latter is above 6 m*M*. In mixtures, the sum of the two is obtained by polarography at the DME. Solid adenosine is then added to the solution and the adenine is determined by voltammetry at the PGE.

THE POLAROGRAPHIC reduction of adenine (I) and its application to the determination of this compound have been described by Smith and Elving.[1,2] Adenosine (II) appears to be polarographically reduced by the same mechanism as is adenine,[3] but as the half-wave potentials are very close, the analysis of mixtures of the two compounds is not possible.


(I)


(II)

Adenine[4] and adenosine[5] can also be oxidized electrochemically at the pyrolytic graphite electrode (PGE). The mechanism[4] and a brief examination of the analytical utility of the oxidation peak of adenine at the PGE have been reported.[6]

In some recent work in this laboratory we found it necessary to be able to determine small quantities of adenine in the presence of fairly large amounts of adenosine, and also on occasion to be able to determine both adenine and adenosine in mixtures of the two compounds.

Methods have been described for the determination of adenine and adenosine in mixtures. Johnstone and Briner[7] and Cerletti and Siliprandi[8] developed methods based on separation of adenine and adenosine by paper chromatography. However, these methods are very slow and were not applicable to the concentration levels of adenine and adenosine in which we were interested.

As the ultraviolet absorption spectra of adenine and adenosine are very similar, their simultaneous spectrophotometric determination is difficult. In addition, it is impossible to determine adenine in the presence of very large amounts of adenosine (*i.e.*, 100-fold) by ultraviolet spectrophotometry.

This paper describes techniques whereby adenine and adenosine can be determined by utilizing the polarographic reduction waves of both compounds at the dropping mercury electrode (DME), and the voltammetric oxidation peak of adenine at the PGE. In order to develop a satisfactory analytical method it was found necessary to investigate in some detail the adsorpion of adenine and adenosine at the PGE, and the effect of adenosine on the extent of adsorption of adenine.

EXPERIMENTAL

Chemicals

Adenine and adenosine were obtained from Nutritional Biochemicals Corp. The acetate buffer pH 4·7 used throughout this work was prepared from reagent grade chemicals and had an ionic strength of 0·5. Water-saturated argon (Linde) was used for deaeration.

Apparatus

Polarograms (DME) were recorded on a Sargent Model XVI Polarograph at a scan-rate of 3·3 mV/sec. Direct current voltammograms at the PGE were recorded with the apparatus described by Dryhurst *et al.*,[9] incorporating a Hewlett-Packard Model 7001A X–Y recorder at a scan rate of 5 mV/sec. Alternating current voltammograms at the PGE were also obtained with the same operational amplifier instrument combined with a Princeton Applied Research Model 121 Lock-in Amplifier/Phase Detector. For a.c. voltammetry a d.c. ramp of 5 mV/sec and a sinusoidal signal of 100 Hz and 10 mV peak-to-peak was used for all experiments. A three-compartment cell maintained at 25 ± 0·1° was used for all experiments and contained a saturated calomel reference electrode (SCE) and a platinum gauze counter-electrode. All potentials are referred to the SCE at 25°C.

The PGE's were machined from small rods of pyrolytic graphite (Super-Temp Company, Santa Fe Springs, Calif.) to a diameter of 4 mm and length *ca.* 10 mm, and were sealed into lengths of 4-mm bore glass tube with Hysol Epoxi-Patch (Hysol Corp., Olean, New York). The electrodes were ground flush with the end of the glass tube.

A conventional dropping mercury electrode was used which had normal *m* and *t* values.

Polarographic procedure

Suitable solutions of adenine, adenosine or mixtures of the two compounds were prepared by diluting appropriate volumes of stock solutions of adenine and adenosine in acetate buffer pH 4·7 with the same buffer solution. Polarograms were run from −1·0 to −1·6 V. The polarogram of pure buffer solution was also recorded, and the limiting currents for the reduction waves were obtained by difference.

Voltammetric procedure

For d.c. voltammetry the PGE was resurfaced before each voltammogram was run, by polishing on a 600-grade silicon carbide paper mounted on a rotating metallographic polishing disc (Buehler Inc., Evanston, Ill.). The surface of the PGE was then washed for 10–15 sec with a fine spray of water. The shaft of the electrode was dried thoroughly and any excess of water remaining on the electrode surface was removed by touching the surface very gently with a soft absorbent paper tissue.

Test solutions were not deaerated. The PGE was inserted into the test solution and after 10 sec at the initial potential (0·4 V for d.c. voltammetry) the voltage scan was started. At least three replicate voltammograms were recorded for each test solution. Voltammograms on background solution were recorded in the same way. The adenine or adenosine peak current was obtained by arithmetically subtracting the observed background current at the peak potential from the test solution peak current.

For a.c. voltammetry it was found that even for pure background solution supporting electrolyte the alternating base current was not very reproducible after each resurfacing of the PGE, no doubt because of variations in the surface roughness and hence in the electrode double-layer capacity.

Accordingly, after resurfacing of the electrode, one set of results was obtained by immersing the electrode in supporting electrolyte, applying the initial potential (0·00 V) for 10 sec and then commencing the scan. The final potential was normally 1·4 or 1·5 V. The first voltammogram was not normally recorded since in general it did not agree with subsequent voltammograms. This is possibly due to the fact that the first trace reflects certain specific surface effects (*e.g.*, surface oxide reduction) which are not observed on the subsequent traces. At the end of the scan the electrode was removed from the cell and the shaft carefully dried but the electrode surface itself was not touched. After 30 sec the electrode was replaced in the cell and the background trace recorded at least three times. Under these conditions the background voltammograms always agreed very closely. The electrode was then removed and treated as just described, except that the background solution in the cell was replaced by the appropriate test solution. After 30 sec the electrode was replaced and the sample trace was recorded at least twice.

Polarographic calibration curves

Calibration curves for the polarographic reduction of adenine and adenosine at the DME in an acetate buffer at pH 4·7 were prepared for concentrations of each compound ranging from *ca.* 0·1 to 1·5 m*M*. Both compounds give straight-line i_1 *vs.* C plots over this concentration range, adenosine giving slightly lower currents.

Voltammetric calibration curve

Concentrations of adenine ranging from *ca.* 0·1 to 1·5 m*M* in acetate buffer at pH 4·7 were made *ca.* 6–6·5 m*M* in adenosine by adding the appropriate amount of solid adenosine to each solution (*i.e.*, for a 25-ml aliquot of an adenine solution 0·045–0·046 g of solid adenosine was added). Voltammetric traces were recorded between 0·4 and 1·25 V. Adenine gives a well-formed peak at 1·10–1·16 V (the peak potential shifts to more positive values with increasing concentration of adenine), and in the presence of 6–6·5 m*M* adenosine a linear relationship between the peak current i_1 and adenine concentration was obtained.

Determination of adenine and adenosine in mixtures

For solutions containing mixtures of up to *ca.* 1·5 m*M* adenine and *ca.* 1·5 m*M* adenosine where both compounds are to be determined, the solution is adjusted to pH 4·7 and ionic strength of about 0·5 with an acetate buffer. An aliquot of the resulting solution is placed in a polarographic cell, thoroughly deaerated with argon and a polarogram at the DME recorded between −1·0 and −1·6 V. The current observed for this polarogram is proportional to the total concentration of adenine plus adenosine.

A second aliquot is then taken and sufficient solid adenosine is weighed into the solution to increase its concentration to 6–6·5 m*M*. After dissolution of the adenosine the solution is placed in a polarographic cell and a voltammogram is run at the stationary PGE between 0·4 and 1·25 V. The height of the peak observed at 1·10–1·16 V is proportional to the adenine concentration.

Thus, the concentration of adenine in the mixture is determined from the height of the voltammetric oxidation peak of adenine in the presence of a large excess of adenosine. The current expected for the polarographic reduction of this amount of adenine is determined from the calibration curve for polarographic reduction of adenine. This current is subtracted from the total polarographic current observed for the adenine–adenosine mixture and hence the current due to adenosine is calculated. The concentration of adenosine is then readily obtained from the adenosine polarographic calibration curve.

RESULTS AND DISCUSSION

Polarography

The pH-dependent half-wave potential for polarographic reduction of adenine at the DME is described by the equation,[3] $E_{1/2} = -0{\cdot}975 - 0{\cdot}084\,\text{pH}$ between pH 1·0 and 6·5. The $E_{1/2}$ for the single, well-formed polarographic wave of adenosine is also pH dependent. Between pH 0 and 4·5, $E_{1/2} = -1{\cdot}040 - 0{\cdot}070\,\text{pH}$ and between pH 4·5 and 6·0, $E_{1/2} = -1{\cdot}180 - 0{\cdot}041\,\text{pH}$.[3] The waves for both compounds are relatively constant in height up to about pH 5, when they begin to decrease sharply with increasing pH and disappear by pH 6–7, since both compounds are only reducible in the protonated form (pK_a of adenine 4·20, pK_a adenosine 3·60). Comparison of the equations for adenine and adenosine reveals that at all pH values where the polarographic waves are observed both compounds have essentially identical $E_{1/2}$ values, *i.e.*, at pH 4·7 both compounds have an $E_{1/2}$ value of −1·37 V.

Adenine and adenosine both gave limiting currents that were linearly proportional to concentration, and which were additive for mixtures.

Voltammetry

Over the normal pH range (0–14) adenine and adenosine give a single pH-dependent voltammetric oxidation peak at the PGE. The adenine peak always occurs at more negative potentials than that of adenosine (Fig. 1). The shift of peak potential with pH is described by the equation $E_p = 1·338 - 0·063$ pH for adenine and $E_p = 1·778 - 0·087$ pH for adenosine at concentrations of *ca.* 0·25 m*M*. However, the peak potentials for both adenine and adenosine are concentration-dependent and shift to more positive values with increasing concentration. Over the approximate concentration range of 0·1–1 m*M* this shift was about 80 mV for both compounds. At below pH 4–5 in buffer solutions containing chloride ion the oxidation peaks of both adenine and adenosine are masked by the facile oxidation of chloride ion in the background electrolyte.

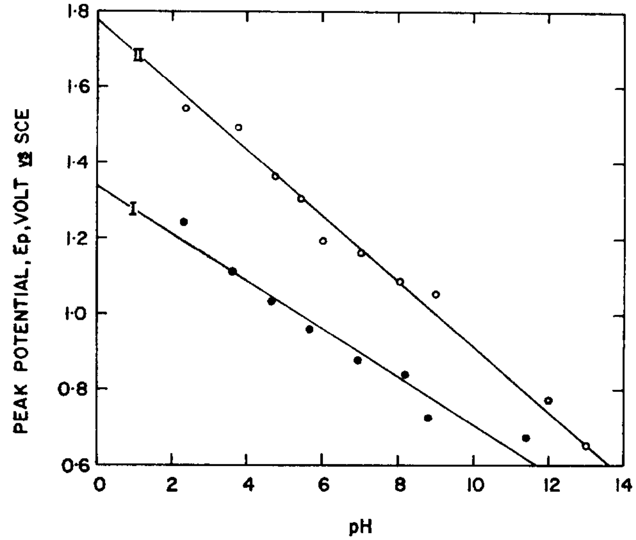


FIG. 1.—Variation of peak potential with pH for the voltammetric oxidation of adenine (I) and adenosine (II) at the PGE at the 0·25 m*M* concentration level.

Both compounds exhibit a rather non-linear relationship between peak current and concentration (Fig. 2), the non-linearity being more pronounced in the case of adenine.

A preliminary examination of the determination of adenine in the presence of adenosine on the basis of the adenine peak current and a calibration curve of the type shown in Fig. 2-I revealed that the adenine concentrations so determined were always very low. Further investigation revealed that addition of adenosine to an adenine solution caused a pronounced decrease in the height of the adenine peak, reaching a constant value of about 55% for a molar ratio of greater than 5:1.

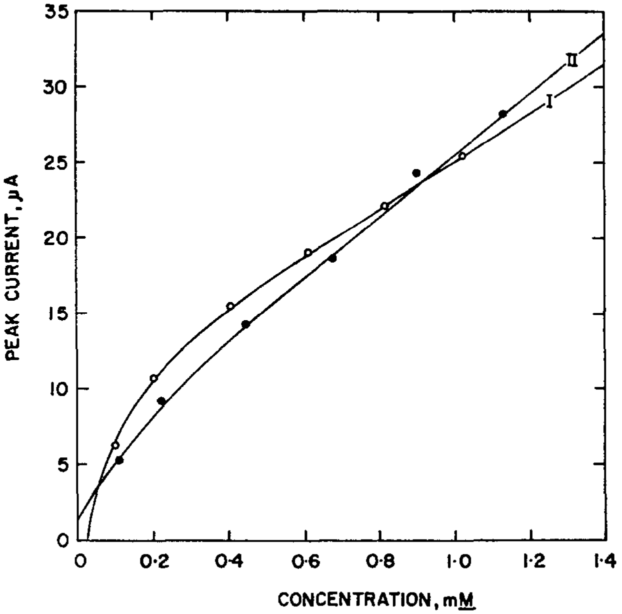


FIG. 2.—Peak current versus concentration relation for the voltammetric oxidation of adenine (I) and adenosine (II) at the PGE.

The non-linear i_p *vs.* C curves for adenine and adenosine suggested that both compounds were adsorbed on the PGE. The fact that the presence of adenosine caused the peak current for adenine to decrease suggested that a competitive adsorption of the two compounds occurred, and that adenosine was displacing part of the adenine from the electrode surface.

In order to investigate further the adsorption of adenine a scan-rate study of the voltammetric oxidation peak of adenine was carried out. This could not be done for adenosine since its oxidation peak occurs so close to background discharge potentials that at scan-rates above *ca.* 20 mV/sec it gives only an inflection on the rise of the background current and accurate measurement of the peak current is impossible.

Earlier studies[4,10] and a.c. voltammetry (*vide infra*) of adenine had revealed that the electrochemical oxidation of adenine is an irreversible process. The theoretical equation for the peak current, i_p (μA) for a linear diffusion-controlled irreversible peak voltammogram at a plane electrode is shown in equation (1).[11,16,13]

$$(i_p)_{\text{irrev}} = 2{\cdot}98 \times 10^5 n\,(\alpha n_a)^{1/2} A D^{1/2} V^{1/2} C \qquad (1)$$

where n is the number of electrons involved in the overall reaction, α the electron transfer coefficient, n_a the number of electrons involved in the rate-controlling electron-transfer process, A the electrode area (cm^2), D the diffusion coefficient of the electroactive species (cm^2/sec), V the voltage scan-rate (V/sec) and C the bulk concentration of the electroactive species (mM). According to this equation, $i_p/ACV^{1/2}$, the peak current function, should be a constant, and a plot of this function *vs.* $V^{1/2}$ (or V) should be a straight line parallel to the $V^{1/2}$ axis. In the case of adenine however the peak-current function shows a pronounced increase with increasing scan-rate (Fig. 3A), typical of an electrode process where the reactant is adsorbed at the electrode surface. In such a

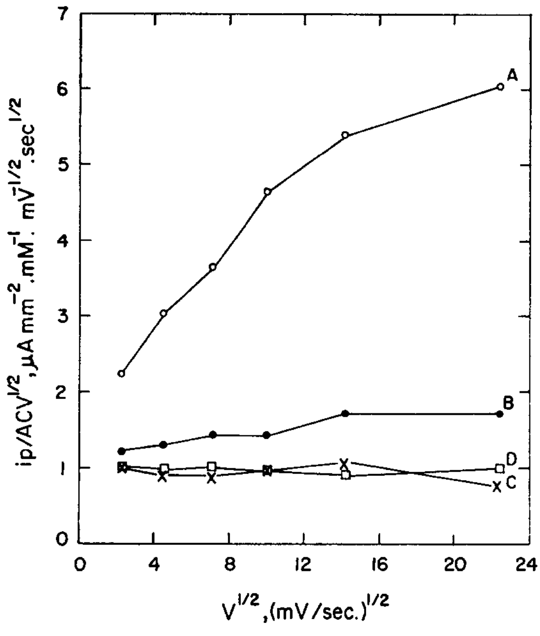


FIG. 3.—Variation of the peak current function, $i_p/ACV^{1/2}$, with the square root of the voltage scan-rate for (A) 0·1025 m*M* adenine, (B) 0·1025 m*M* adenine with 1·00 m*M* adenosine, (C) 0·1025 m*M* adenine with 2·77 m*M* adenosine and (D) 0·2228 m*M* adenine with 6·27 m*M* adenosine. Acetate buffer pH 4·7. PGE geometric area: 12·5 mm².

case the amount of adsorbed material and hence of charge flow (at least in the case of a perfectly reproducible electrode surface) is constant, and the amount of material diffusing to the electrode surface is time dependent with the result that as the scan-rate increases, the contribution from diffusing material decreases with respect to the amount of adsorbed material reacting at the electrode surface, and the peak-current function increases.[14]

On addition of adenosine to adenine in 10:1 molar ratio the peak-current function decreased markedly (Fig. 3B) and the variation of the peak-current function became more in line with that expected for a diffusion-controlled reaction. Addition of a 30:1 molar ratio of adenosine resulted in a further slight decrease in the peak-current function, particularly at higher scan-rates (Fig. 3CD), but the effect was very small at the lowest scan rates studied (5 mV/sec). It was not possible to study the peak current for adenine in the presence of large amounts of adenosine at scan-rates much above 500 mV/sec because the peak potential for adenine shifts to more positive values with increasing scan-rate and the peak merges with the background discharge (from oxidation of the adenosine).

Values of the diffusion coefficient as calculated from relevant polarographic data ($1{\cdot}87 \times 10^{-3}$ mm²/sec) and of αn_a calculated according to

$$E_p - E_{p/2} = 0{\cdot}048/\alpha n_a \qquad (2)$$

were inserted into (1) to obtain theoretical peak currents of 1·55 and 2·32 $\mu A \cdot mm^{-2} \cdot mM^{-1} \cdot mV^{-1/2} \cdot sec^{1/2}$ assuming a four- or a six-electron oxidation respectively. Coulometric evidence suggests that six electrons are involved per molecule of adenine, but in the presence of a large amount of adenosine as is here the case, the experimental value of around unity for the peak current (Fig. 3) would be more in agreement with a four-electron reaction. It should be stressed that the αn_a value cannot be determined accurately since the adenine peak lies so close to the background discharge, and a close agreement between the theoretical and experimental values is not to be expected.

Alternating current voltammetry

A qualitative technique for observing the regions of potential where adsorption of organic molecules takes place at a dropping mercury electrode is a.c. polarography. In the potential regions where adsorption occurs, pronounced depressions of the alternating base current occur owing to a decrease of the double-layer capacity of the electrode.[15] A few reports of a.c. techniques at solid or stationary electrodes have appeared[16-20] but only that of Delahay and Trachtenberg[21] at stationary mercury electrodes has dealt specifically with adsorption effects. Alternating current voltammograms of adenine and adenosine and mixtures of the two are presented in Fig. 4. It is clear from the voltammograms shown in Figs. 4A and 4B that both adenine and adenosine markedly depress the alternating base current over the whole potential range examined. Since the base current for both compounds is depressed at potentials more negative than the DC peak it is obvious that both adenine and adenosine are adsorbed at the PGE. Both compounds also exhibit a rather pronounced pit, or well potentials corresponding to the rising portion of the d.c. peak. The depression of the base current at potentials more positive than the d.c. peak appears to be more pronounced than at more negative ones, indicating that one of the products of the oxidation of these compounds is quite strongly adsorbed at the PGE. The a.c. voltammetric results are clearly in agreement with the results of the scan-rate and sweep-rate studies on adenine, *i.e.*, that adenine is adsorbed at the PGE. The absence of any faradaic a.c. peaks at potentials in the vicinity of the d.c. peaks for both adenine and adenosine confirms the irreversible nature of these electrode processes.[4,5]

Figure 4C shows that making a 6·3m*M* solution of adenosine in acetate buffer at pH 4·7 1m*M* in adenine still causes an appreciable base current depression at potentials more negative and more positive than the adenine d.c. peak, especially at the more positive potentials. However this depression is not as pronounced as it is in the absence of adenosine and indeed for 20:1 or 30:1 molar ratios of adenosine to adenine, it is not observed by a.c. techniques.

The conclusion that can be drawn from the qualitative a.c., sweep-rate and concentration studies is that both adenine and adenosine and at least one of their oxidation products are adsorbed at the PGE. In the presence of large amounts of adenosine, adsorbed adenine is largely displaced from the electrode surface and the voltammetric oxidation of adenine becomes effectively diffusion-controlled.

Development of analytical methods

The DME studies on adenine, adenosine and mixtures of the two show that the polarographic limiting current is directly proportional to the sum of the concentrations of the two bases. In contrast, at the PGE adenine and adenosine are both adsorbed and as a result of competitive adsorption the peak current for adenine is dependent on the concentration of adenosine present, though at sufficiently large concentrations of adenosine, adenine is to a considerable extent displaced from the electrode surface

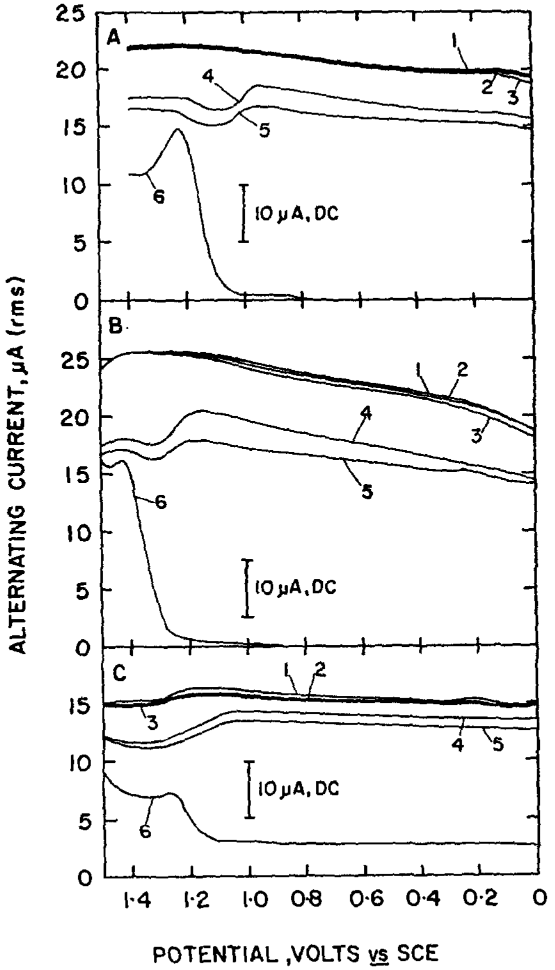


FIG. 4.—Alternating current voltammograms at the PGE in acetate buffer at pH 4·7 of A, 1 m*M* adenine; B, 1 m*M* adenosine. Scans 1, 2, 3 are a.c. background traces, scans 4 and 5 are a.c. traces in the presence of adenine or adenosine, scan 6 is a d.c. voltammogram. C: Scans 1, 2, 3 are of 6·27 m*M* adenosine in acetate buffer pH 4·7, scans 4 and 5 are 6·27 m*M* adenosine plus 1 m*M* adenine, scan 6 is a d.c. voltammogram. Scan rate: 5 mV/sec; alternating voltage 10 mV peak-to-peak, 100 Hz. PGE geometric area: 12·5 mm^2.

and its oxidation becomes a diffusion-controlled process. For a quantitative determination of adenine by voltammetric oxidation large concentration ratios should be used, with a maximum adenine concentration around 1m*M* (approaching its limit of solubility).

Typical i_p *vs*. *C* curves for adenine in the presence of approximately 3m*M* and 6m*M* adenosine are clearly linear but a slightly lower current is observed in the presence of the higher adenosine concentration. In view of the linearity of the latter i_p *vs*. *C* plot over a wide range of molar ratios from 8 to 156 it was felt that accurate determinations of adenine could be performed simply by adding sufficient solid adenosine to adenine–adenosine mixtures to ensure at least a 6–7 fold molar excess of it was present.

In order to test the methods developed, some mixtures of adenine and adenosine in acetate buffer at pH 4·7 were examined. The samples were first analysed polarographically, then solid adenosine was added to the test solutions sufficient to make them *ca.* 6–7m*M* in adenosine. The concentration of adenine was then determined from the height of the resulting voltammetric oxidation peak of adenine at the PGE. Typical analytical results are presented in Table I. Once the calibration curves have been obtained a total analysis of the adenine and adenosine present in a sample can be completed in at most 15 min.

TABLE I.—TYPICAL RESULTS FOR THE ELECTROCHEMICAL DETERMINATION OF MIXTURES OF ADENINE AND ADENOSINE.

Taken, m*M*		Found, m*M*	
Adenine	Adenosine	Adenine	Adenosine
0·098	1·12	0·08	1·14
0·29	0·92	0·30	0·85
0·49	0·73	0·52	0·67
0·93	0·29	0·90	0·29
0·37	0·24	0·37	0·26

CONCLUSION

By a combination of polarography at the DME and voltammetry at the PGE a rapid and reasonably accurate analysis for adenine and adenosine in mixtures is possible. No previously reported method is capable of determining adenine in the pressure of such large amounts of adenosine.

The studies reported in this paper have utilized an acetate buffer at pH 4·7 as the background electrolyte system. A very brief examination of the adenine–adenosine system at lower pH values in acetate buffers or with sulphuric acid-potassium sulphate supporting electrolyte systems revealed that similar results may be obtained. Above pH 6 the polarographic waves of adenine and adenosine become small and kinetically controlled, and utimately disappear at about pH 7, with the result that the polarographic procedure for the determination of the total adenine plus adenosine can no longer be used.

However, the voltammetric oxidation peaks of adenine and of adenosine at the PGE persist to a very high pH, and hence the adenine concentration could still be determined. If it were necessary to determine the adenosine and adenine concentration at above pH 6 it should be possible to determine the total base concentrations by ultraviolet absorption spectrophotometry and the adenine concentration from its voltammetric oxidation peak at the PGE in the presence of a large excess of adenosine.

Acknowledgement—The author would like to express his thanks to the National Science Foundation for financial support of the work.

Zusammenfassung—Adenin und Adenosin lassen sich aus wäßriger Lösung bei pH 4·7 polarographisch an der Quecksilbertropfelektrode (DME) beim selben Halbstufenpotential reduzieren. An einer Elektrode aus Pyrolysegraphit (PGE) sind beide voltammetrisch oxidierbar, Adenosin jedoch bei höherem Potential. Die konkurrierende Adsorption beider Verbindungen an der PGE führt dazu, daß der Adeninpeak beim Registrieren der voltammetrischen Oxidation in Gegenwart von Adenosin kleiner wird und bei einer Adenosinkonzentration über 6 m*M* einen konstanten Wert erreicht. In Gemischen wird die Summe beider Verbindungen durch Polarographie an der DME erhalten. Dann wird festes Adenosin zur Lösung gegeben und Adenin durch Voltammetrie an der PGE bestimmt.

Résumé—L'adénine et l'adénosine sont réductibles polarographiquement en solution aqueuse à pH 4,7 à l'électrode à goutte de mercure au même $E_{1/2}$, et sont également oxydables voltammétriquement à l'élec trode de toile de platine, mais à des potentiels différents, l'adénosine aux potentiels plus élevés. L'adsorption compétitive des deux composés sur l'électrode de toile de platine a pour conséquence un abaissement dans le pic d'oxydation voltammétrique de l'adénine en la présence d'adénosine, atteignant une valeur constante lorsque la concentration de cette dernière est supérieure à 6 m*M*. Dans les mélanges, la somme des deux est obtenue par polarographie à l'électrode à goutte de mercure. On ajoute alors de l'adénosine solide à la solution et l'on dose l'adénine par voltammétrie a l'électrode de toile de platine.

REFERENCES

1. D. L. Smith and P. J. Elving, *J. Am. Chem. Soc.*, 1962, **84**, 1412.
2. *Idem*, *Anal. Chem.*, 1962, **34**, 930.
3. B. Janik and P. J. Elving, *Chem. Revs.*, 1968, **68**, 295.
4. G. Dryhurst and P. J. Elving, *J. Electrochem. Soc.*, 1968, **115**, 1014.
5. G. Dryhurst, unpublished work.
6. G. Dryhurst and P. J. Elving, *Talanta*, 1969, **16**, 855.
7. B. M. Johnstone and G. P. Briner, *Nature*, 1959, **183**, 681.
8. P. Cerletti and N. Siliprandi, *Ric. Sci.*, 1955, **25**, 208.
9. G. Dryhurst, M. Rosen and P. J. Elving, *Anal. Chim. Acta*, 1968, **42**, 143.
10. G. Dryhurst, *J. Electrochem. Soc.*, 1969, **116**, 1411.
11. R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
12. P. Delahay, *J. Am. Chem. Soc.*, 1953, **75**, 1190.
13. M. Matsuda and Y. Ayabe, *Z. Elektrochem.*, 1955, **59**, 494.
14. R. H. Wopschall and I. Shain, *Anal. Chem.*, 1967, **39**, 1514.
15. B. Breyer and H. H. Bauer, *Alternating Current Polarography and Tensammetry*, Interscience New York, 1963.
16. D. E. Smith and W. H. Reinmuth, *Anal. Chem.*, 1960, **32**, 1892.
17. A. J. Juliard, *J. Electroanal. Chem.*, 1959, **1**, 101.
18. W. L. Underkofler and I. Shain, *Anal. Chem.*, 1965, **37**, 218.
19. D. N. Walker, R. N. Adams and A. L. Juliard, *ibid.*, 1960, **32**, 1526.
20. H. H. Bauer, M. S. Spritzer and P. J. Elving, *J. Electroanal. Chem.*, 1968, **17**, 299.
21. P. Delahay and I. Trachtenberg, *J. Am. Chem. Soc.*, 1957, **79**, 2355.

Talanta, 1972, Vol. 19, pp. 769 to 787. Pergamon Press. Printed in Northern Ireland

ELECTROCHEMICAL DETERMINATION OF ADENINE AND ADENOSINE

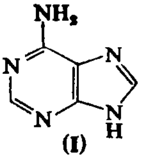
ADSORPTION OF ADENINE AND ADENOSINE AT THE PYROLYTIC GRAPHITE ELECTRODE

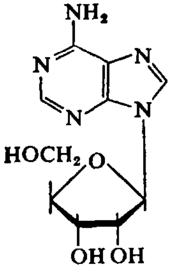
GLENN DRYHURST
Department of Chemistry, University of Oklahoma, Norman, Oklahoma, 73069, U.S.A.

(*Received* 12 *July* 1971. *Accepted* 30 *October* 1971)

Summary—Adenine and adenosine are polarographically reducible from aqueous solution at pH 4·7 at the DME at the same $E_{1/2}$, and are also voltammetrically oxidizable at the PGE, but at different potentials, adenosine at higher potentials. Competitive adsorption of both compounds at the PGE results in a decrease in the scanning voltammetric oxidation peak of adenine in the presence of adenosine, reaching a constant value when the concentration of the latter is above 6 m*M*. In mixtures, the sum of the two is obtained by polarography at the DME. Solid adenosine is then added to the solution and the adenine is determined by voltammetry at the PGE.

THE POLAROGRAPHIC reduction of adenine (I) and its application to the determination of this compound have been described by Smith and Elving.[1,2] Adenosine (II) appears to be polarographically reduced by the same mechanism as is adenine,[3] but as the half-wave potentials are very close, the analysis of mixtures of the two compounds is not possible.


(I)


(II)

Adenine[4] and adenosine[5] can also be oxidized electrochemically at the pyrolytic graphite electrode (PGE). The mechanism[4] and a brief examination of the analytical utility of the oxidation peak of adenine at the PGE have been reported.[6]

In some recent work in this laboratory we found it necessary to be able to determine small quantities of adenine in the presence of fairly large amounts of adenosine, and also on occasion to be able to determine both adenine and adenosine in mixtures of the two compounds.

Methods have been described for the determination of adenine and adenosine in mixtures. Johnstone and Briner[7] and Cerletti and Siliprandi[8] developed methods based on separation of adenine and adenosine by paper chromatography. However, these methods are very slow and were not applicable to the concentration levels of adenine and adenosine in which we were interested.

As the ultraviolet absorption spectra of adenine and adenosine are very similar, their simultaneous spectrophotometric determination is difficult. In addition, it is impossible to determine adenine in the presence of very large amounts of adenosine (*i.e.*, 100-fold) by ultraviolet spectrophotometry.

This paper describes techniques whereby adenine and adenosine can be determined by utilizing the polarographic reduction waves of both compounds at the dropping mercury electrode (DME), and the voltammetric oxidation peak of adenine at the PGE. In order to develop a satisfactory analytical method it was found necessary to investigate in some detail the adsorpion of adenine and adenosine at the PGE, and the effect of adenosine on the extent of adsorption of adenine.

EXPERIMENTAL

Chemicals

Adenine and adenosine were obtained from Nutritional Biochemicals Corp. The acetate buffer pH 4·7 used throughout this work was prepared from reagent grade chemicals and had an ionic strength of 0·5. Water-saturated argon (Linde) was used for deaeration.

Apparatus

Polarograms (DME) were recorded on a Sargent Model XVI Polarograph at a scan-rate of 3·3 mV/sec. Direct current voltammograms at the PGE were recorded with the apparatus described by Dryhurst *et al.*,[9] incorporating a Hewlett-Packard Model 7001A X–Y recorder at a scan rate of 5 mV/sec. Alternating current voltammograms at the PGE were also obtained with the same operational amplifier instrument combined with a Princeton Applied Research Model 121 Lock-in Amplifier/Phase Detector. For a.c. voltammetry a d.c. ramp of 5 mV/sec and a sinusoidal signal of 100 Hz and 10 mV peak-to-peak was used for all experiments. A three-compartment cell maintained at 25 ± 0·1° was used for all experiments and contained a saturated calomel reference electrode (SCE) and a platinum gauze counter-electrode. All potentials are referred to the SCE at 25°C.

The PGE's were machined from small rods of pyrolytic graphite (Super-Temp Company, Santa Fe Springs, Calif.) to a diameter of 4 mm and length *ca.* 10 mm, and were sealed into lengths of 4-mm bore glass tube with Hysol Epoxi-Patch (Hysol Corp., Olean, New York). The electrodes were ground flush with the end of the glass tube.

A conventional dropping mercury electrode was used which had normal *m* and *t* values.

Polarographic procedure

Suitable solutions of adenine, adenosine or mixtures of the two compounds were prepared by diluting appropriate volumes of stock solutions of adenine and adenosine in acetate buffer pH 4·7 with the same buffer solution. Polarograms were run from −1·0 to −1·6 V. The polarogram of pure buffer solution was also recorded, and the limiting currents for the reduction waves were obtained by difference.

Voltammetric procedure

For d.c. voltammetry the PGE was resurfaced before each voltammogram was run, by polishing on a 600-grade silicon carbide paper mounted on a rotating metallographic polishing disc (Buehler Inc., Evanston, Ill.). The surface of the PGE was then washed for 10–15 sec with a fine spray of water. The shaft of the electrode was dried thoroughly and any excess of water remaining on the electrode surface was removed by touching the surface very gently with a soft absorbent paper tissue.

Test solutions were not deaerated. The PGE was inserted into the test solution and after 10 sec at the initial potential (0·4 V for d.c. voltammetry) the voltage scan was started. At least three replicate voltammograms were recorded for each test solution. Voltammograms on background solution were recorded in the same way. The adenine or adenosine peak current was obtained by arithmetically subtracting the observed background current at the peak potential from the test solution peak current.

For a.c. voltammetry it was found that even for pure background solution supporting electrolyte the alternating base current was not very reproducible after each resurfacing of the PGE, no doubt because of variations in the surface roughness and hence in the electrode double-layer capacity.

Accordingly, after resurfacing of the electrode, one set of results was obtained by immersing the electrode in supporting electrolyte, applying the initial potential (0·00 V) for 10 sec and then commencing the scan. The final potential was normally 1·4 or 1·5 V. The first voltammogram was not normally recorded since in general it did not agree with subsequent voltammograms. This is possibly due to the fact that the first trace reflects certain specific surface effects (*e.g.*, surface oxide reduction) which are not observed on the subsequent traces. At the end of the scan the electrode was removed from the cell and the shaft carefully dried but the electrode surface itself was not touched. After 30 sec the electrode was replaced in the cell and the background trace recorded at least three times. Under these conditions the background voltammograms always agreed very closely. The electrode was then removed and treated as just described, except that the background solution in the cell was replaced by the appropriate test solution. After 30 sec the electrode was replaced and the sample trace was recorded at least twice.

Polarographic calibration curves

Calibration curves for the polarographic reduction of adenine and adenosine at the DME in an acetate buffer at pH 4·7 were prepared for concentrations of each compound ranging from *ca.* 0·1 to 1·5 m*M*. Both compounds give straight-line i_l *vs.* C plots over this concentration range, adenosine giving slightly lower currents.

Voltammetric calibration curve

Concentrations of adenine ranging from *ca.* 0·1 to 1·5 m*M* in acetate buffer at pH 4·7 were made *ca.* 6–6·5 m*M* in adenosine by adding the appropriate amount of solid adenosine to each solution (*i.e.*, for a 25-ml aliquot of an adenine solution 0 045–0 046 g of solid adenosine was added). Voltammetric traces were recorded between 0·4 and 1·25 V. Adenine gives a well-formed peak at 1·10–1·16 V (the peak potential shifts to more positive values with increasing concentration of adenine), and in the presence of 6–6·5 m*M* adenosine a linear relationship between the peak current i_l and adenine concentration was obtained.

Determination of adenine and adenosine in mixtures

For solutions containing mixtures of up to *ca.* 1·5 m*M* adenine and *ca.* 1·5 m*M* adenosine where both compounds are to be determined, the solution is adjusted to pH 4·7 and ionic strength of about 0·5 with an acetate buffer. An aliquot of the resulting solution is placed in a polarographic cell, thoroughly deaerated with argon and a polarogram at the DME recorded between −1·0 and −1·6 V. The current observed for this polarogram is proportional to the total concentration of adenine plus adenosine.

A second aliquot is then taken and sufficient solid adenosine is weighed into the solution to increase its concentration to 6–6·5 m*M*. After dissolution of the adenosine the solution is placed in a polarographic cell and a voltammogram is run at the stationary PGE between 0·4 and 1·25 V. The height of the peak observed at 1·10–1·16 V is proportional to the adenine concentration.

Thus, the concentration of adenine in the mixture is determined from the height of the voltammetric oxidation peak of adenine in the presence of a large excess of adenosine. The current expected for the polarographic reduction of this amount of adenine is determined from the calibration curve for polarographic reduction of adenine. This current is subtracted from the total polarographic current observed for the adenine–adenosine mixture and hence the current due to adenosine is calculated. The concentration of adenosine is then readily obtained from the adenosine polarographic calibration curve.

RESULTS AND DISCUSSION

Polarography

The pH-dependent half-wave potential for polarographic reduction of adenine at the DME is described by the equation,[3] $E_{1/2} = -0{\cdot}975 - 0{\cdot}084\,\mathrm{pH}$ between pH 1·0 and 6·5. The $E_{1/2}$ for the single, well-formed polarographic wave of adenosine is also pH dependent. Between pH 0 and 4·5, $E_{1/2} = -1{\cdot}040 - 0{\cdot}070\,\mathrm{pH}$ and between pH 4·5 and 6·0, $E_{1/2} = -1{\cdot}180 - 0{\cdot}041\,\mathrm{pH}$.[3] The waves for both compounds are relatively constant in height up to about pH 5, when they begin to decrease sharply with increasing pH and disappear by pH 6–7, since both compounds are only reducible in the protonated form (pK_a of adenine 4·20, pK_a adenosine 3·60). Comparison of the equations for adenine and adenosine reveals that at all pH values where the polarographic waves are observed both compounds have essentially identical $E_{1/2}$ values, *i.e.*, at pH 4·7 both compounds have an $E_{1/2}$ value of −1·37 V.

Adenine and adenosine both gave limiting currents that were linearly proportional to concentration, and which were additive for mixtures.

Voltammetry

Over the normal pH range (0–14) adenine and adenosine give a single pH-dependent voltammetric oxidation peak at the PGE. The adenine peak always occurs at more negative potentials than that of adenosine (Fig. 1). The shift of peak potential with pH is described by the equation $E_p = 1{\cdot}338 - 0{\cdot}063$ pH for adenine and $E_p = 1{\cdot}778 - 0{\cdot}087$ pH for adenosine at concentrations of *ca.* 0·25 m*M*. However, the peak potentials for both adenine and adenosine are concentration-dependent and shift to more positive values with increasing concentration. Over the approximate concentration range of 0·1–1 m*M* this shift was about 80 mV for both compounds. At below pH 4–5 in buffer solutions containing chloride ion the oxidation peaks of both adenine and adenosine are masked by the facile oxidation of chloride ion in the background electrolyte.

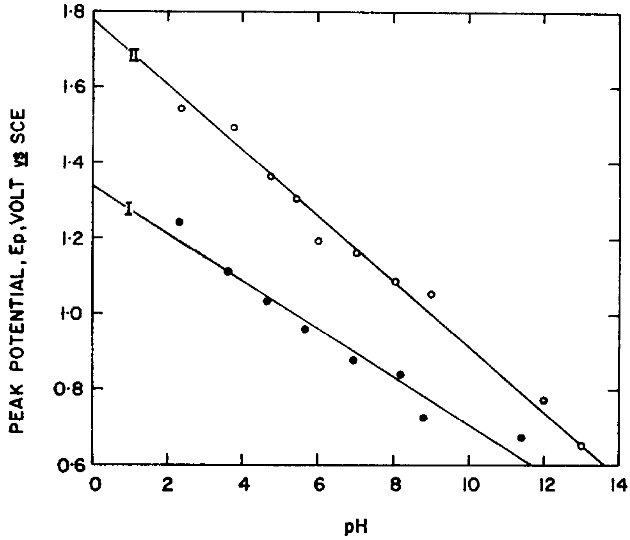


FIG. 1.—Variation of peak potential with pH for the voltammetric oxidation of adenine (I) and adenosine (II) at the PGE at the 0·25 m*M* concentration level.

Both compounds exhibit a rather non-linear relationship between peak current and concentration (Fig. 2), the non-linearity being more pronounced in the case of adenine.

A preliminary examination of the determination of adenine in the presence of adenosine on the basis of the adenine peak current and a calibration curve of the type shown in Fig. 2-I revealed that the adenine concentrations so determined were always very low. Further investigation revealed that addition of adenosine to an adenine solution caused a pronounced decrease in the height of the adenine peak, reaching a constant value of about 55% for a molar ratio of greater than 5:1.

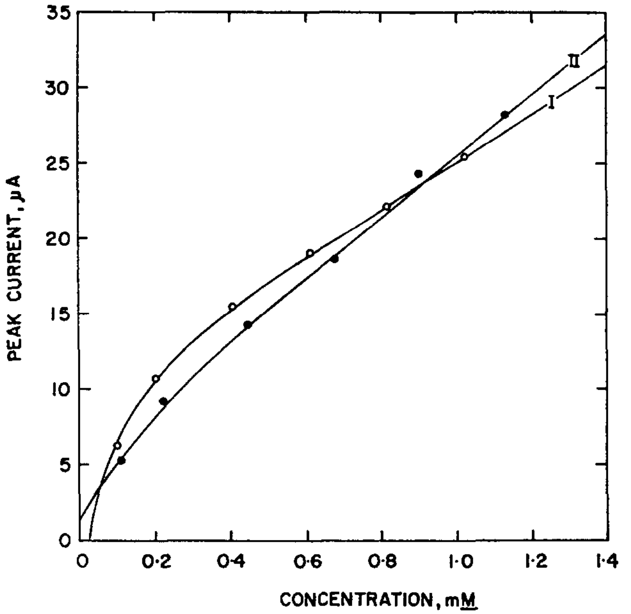


FIG. 2.—Peak current versus concentration relation for the voltammetric oxidation of adenine (I) and adenosine (II) at the PGE.

The non-linear i_p *vs.* C curves for adenine and adenosine suggested that both compounds were adsorbed on the PGE. The fact that the presence of adenosine caused the peak current for adenine to decrease suggested that a competitive adsorption of the two compounds occurred, and that adenosine was displacing part of the adenine from the electrode surface.

In order to investigate further the adsorption of adenine a scan-rate study of the voltammetric oxidation peak of adenine was carried out. This could not be done for adenosine since its oxidation peak occurs so close to background discharge potentials that at scan-rates above *ca.* 20 mV/sec it gives only an inflection on the rise of the background current and accurate measurement of the peak current is impossible.

Earlier studies[4,10] and a.c. voltammetry (*vide infra*) of adenine had revealed that the electrochemical oxidation of adenine is an irreversible process. The theoretical equation for the peak current, i_p (μA) for a linear diffusion-controlled irreversible peak voltammogram at a plane electrode is shown in equation (1).[11,16,13]

$$(i_p)_{\text{irrev}} = 2{\cdot}98 \times 10^5 n\,(\alpha n_a)^{1/2} A D^{1/2} V^{1/2} C \qquad (1)$$

where n is the number of electrons involved in the overall reaction, α the electron transfer coefficient, n_a the number of electrons involved in the rate-controlling electron-transfer process, A the electrode area (cm^2), D the diffusion coefficient of the electroactive species (cm^2/sec), V the voltage scan-rate (V/sec) and C the bulk concentration of the electroactive species (mM). According to this equation, $i_p/ACV^{1/2}$, the peak current function, should be a constant, and a plot of this function *vs.* $V^{1/2}$ (or V) should be a straight line parallel to the $V^{1/2}$ axis. In the case of adenine however the peak-current function shows a pronounced increase with increasing scan-rate (Fig. 3A), typical of an electrode process where the reactant is adsorbed at the electrode surface. In such a

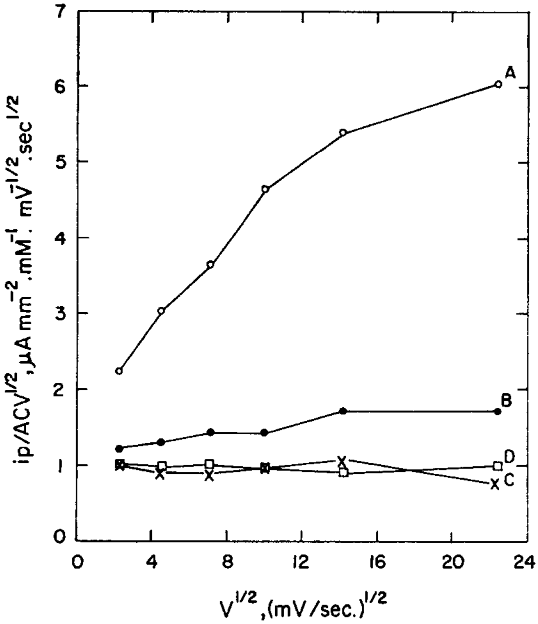


FIG. 3.—Variation of the peak current function, $i_p/ACV^{1/2}$, with the square root of the voltage scan-rate for (A) 0·1025 m*M* adenine, (B) 0·1025 m*M* adenine with 1·00 m*M* adenosine, (C) 0·1025 m*M* adenine with 2·77 m*M* adenosine and (D) 0·2228 m*M* adenine with 6·27 m*M* adenosine. Acetate buffer pH 4·7. PGE geometric area: 12·5 mm².

case the amount of adsorbed material and hence of charge flow (at least in the case of a perfectly reproducible electrode surface) is constant, and the amount of material diffusing to the electrode surface is time dependent with the result that as the scan-rate increases, the contribution from diffusing material decreases with respect to the amount of adsorbed material reacting at the electrode surface, and the peak-current function increases.[14]

On addition of adenosine to adenine in 10:1 molar ratio the peak-current function decreased markedly (Fig. 3B) and the variation of the peak-current function became more in line with that expected for a diffusion-controlled reaction. Addition of a 30:1 molar ratio of adenosine resulted in a further slight decrease in the peak-current function, particularly at higher scan-rates (Fig. 3CD), but the effect was very small at the lowest scan rates studied (5 mV/sec). It was not possible to study the peak current for adenine in the presence of large amounts of adenosine at scan-rates much above 500 mV/sec because the peak potential for adenine shifts to more positive values with increasing scan-rate and the peak merges with the background discharge (from oxidation of the adenosine).

Values of the diffusion coefficient as calculated from relevant polarographic data ($1{\cdot}87 \times 10^{-3}$ mm²/sec) and of αn_a calculated according to

$$E_p - E_{p/2} = 0{\cdot}048/\alpha n_a \qquad (2)$$

were inserted into (1) to obtain theoretical peak currents of 1·55 and 2·32 $\mu A \cdot mm^{-2} \cdot mM^{-1} \cdot mV^{-1/2} \cdot sec^{1/2}$ assuming a four- or a six-electron oxidation respectively. Coulometric evidence suggests that six electrons are involved per molecule of adenine, but in the presence of a large amount of adenosine as is here the case, the experimental value of around unity for the peak current (Fig. 3) would be more in agreement with a four-electron reaction. It should be stressed that the αn_a value cannot be determined accurately since the adenine peak lies so close to the background discharge, and a close agreement between the theoretical and experimental values is not to be expected.

Alternating current voltammetry

A qualitative technique for observing the regions of potential where adsorption of organic molecules takes place at a dropping mercury electrode is a.c. polarography. In the potential regions where adsorption occurs, pronounced depressions of the alternating base current occur owing to a decrease of the double-layer capacity of the electrode.[15] A few reports of a.c. techniques at solid or stationary electrodes have appeared[16–20] but only that of Delahay and Trachtenberg[21] at stationary mercury electrodes has dealt specifically with adsorption effects. Alternating current voltammograms of adenine and adenosine and mixtures of the two are presented in Fig. 4. It is clear from the voltammograms shown in Figs. 4A and 4B that both adenine and adenosine markedly depress the alternating base current over the whole potential range examined. Since the base current for both compounds is depressed at potentials more negative than the DC peak it is obvious that both adenine and adenosine are adsorbed at the PGE. Both compounds also exhibit a rather pronounced pit, or well potentials corresponding to the rising portion of the d.c. peak. The depression of the base current at potentials more positive than the d.c. peak appears to be more pronounced than at more negative ones, indicating that one of the products of the oxidation of these compounds is quite strongly adsorbed at the PGE. The a.c. voltammetric results are clearly in agreement with the results of the scan-rate and sweep-rate studies on adenine, *i.e.*, that adenine is adsorbed at the PGE. The absence of any faradaic a.c. peaks at potentials in the vicinity of the d.c. peaks for both adenine and adenosine confirms the irreversible nature of these electrode processes.[4,5]

Figure 4C shows that making a 6·3m*M* solution of adenosine in acetate buffer at pH 4·7 1m*M* in adenine still causes an appreciable base current depression at potentials more negative and more positive than the adenine d.c. peak, especially at the more positive potentials. However this depression is not as pronounced as it is in the absence of adenosine and indeed for 20:1 or 30:1 molar ratios of adenosine to adenine, it is not observed by a.c. techniques.

The conclusion that can be drawn from the qualitative a.c., sweep-rate and concentration studies is that both adenine and adenosine and at least one of their oxidation products are adsorbed at the PGE. In the presence of large amounts of adenosine, adsorbed adenine is largely displaced from the electrode surface and the voltammetric oxidation of adenine becomes effectively diffusion-controlled.

Development of analytical methods

The DME studies on adenine, adenosine and mixtures of the two show that the polarographic limiting current is directly proportional to the sum of the concentrations of the two bases. In contrast, at the PGE adenine and adenosine are both adsorbed and as a result of competitive adsorption the peak current for adenine is dependent on the concentration of adenosine present, though at sufficiently large concentrations of adenosine, adenine is to a considerable extent displaced from the electrode surface

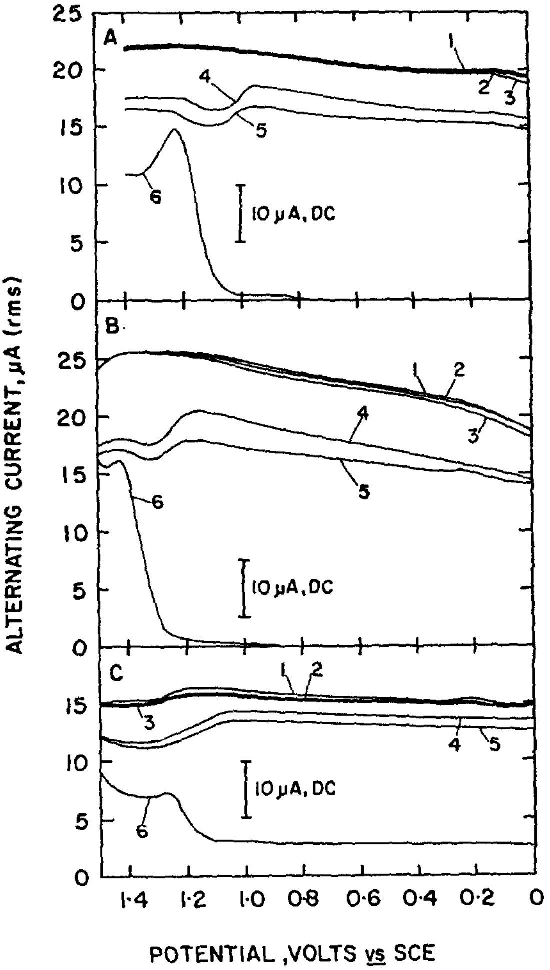


FIG. 4.—Alternating current voltammograms at the PGE in acetate buffer at pH 4·7 of A, 1 m*M* adenine; B, 1 m*M* adenosine. Scans 1, 2, 3 are a.c. background traces, scans 4 and 5 are a.c. traces in the presence of adenine or adenosine, scan 6 is a d.c. voltammogram. C: Scans 1, 2, 3 are of 6·27 m*M* adenosine in acetate buffer pH 4·7, scans 4 and 5 are 6·27 m*M* adenosine plus 1 m*M* adenine, scan 6 is a d.c. voltammogram. Scan rate: 5 mV/sec; alternating voltage 10 mV peak-to-peak, 100 Hz. PGE geometric area: 12·5 mm².

and its oxidation becomes a diffusion-controlled process. For a quantitative determination of adenine by voltammetric oxidation large concentration ratios should be used, with a maximum adenine concentration around 1m*M* (approaching its limit of solubility).

Typical i_p *vs*. *C* curves for adenine in the presence of approximately 3m*M* and 6m*M* adenosine are clearly linear but a slightly lower current is observed in the presence of the higher adenosine concentration. In view of the linearity of the latter i_p *vs*. *C* plot over a wide range of molar ratios from 8 to 156 it was felt that accurate determinations of adenine could be performed simply by adding sufficient solid adenosine to adenine–adenosine mixtures to ensure at least a 6–7 fold molar excess of it was present.

In order to test the methods developed, some mixtures of adenine and adenosine in acetate buffer at pH 4·7 were examined. The samples were first analysed polarographically, then solid adenosine was added to the test solutions sufficient to make them *ca.* 6–7m*M* in adenosine. The concentration of adenine was then determined from the height of the resulting voltammetric oxidation peak of adenine at the PGE. Typical analytical results are presented in Table I. Once the calibration curves have been obtained a total analysis of the adenine and adenosine present in a sample can be completed in at most 15 min.

TABLE I.—TYPICAL RESULTS FOR THE ELECTROCHEMICAL DETERMINATION OF MIXTURES OF ADENINE AND ADENOSINE.

Taken, m*M*		Found, m*M*	
Adenine	Adenosine	Adenine	Adenosine
0·098	1·12	0·08	1·14
0·29	0·92	0·30	0·85
0·49	0·73	0·52	0·67
0·93	0·29	0·90	0·29
0·37	0·24	0·37	0·26

CONCLUSION

By a combination of polarography at the DME and voltammetry at the PGE a rapid and reasonably accurate analysis for adenine and adenosine in mixtures is possible. No previously reported method is capable of determining adenine in the pressure of such large amounts of adenosine.

The studies reported in this paper have utilized an acetate buffer at pH 4·7 as the background electrolyte system. A very brief examination of the adenine–adenosine system at lower pH values in acetate buffers or with sulphuric acid-potassium sulphate supporting electrolyte systems revealed that similar results may be obtained. Above pH 6 the polarographic waves of adenine and adenosine become small and kinetically controlled, and utimately disappear at about pH 7, with the result that the polarographic procedure for the determination of the total adenine plus adenosine can no longer be used.

However, the voltammetric oxidation peaks of adenine and of adenosine at the PGE persist to a very high pH, and hence the adenine concentration could still be determined. If it were necessary to determine the adenosine and adenine concentration at above pH 6 it should be possible to determine the total base concentrations by ultraviolet absorption spectrophotometry and the adenine concentration from its voltammetric oxidation peak at the PGE in the presence of a large excess of adenosine.

Acknowledgement—The author would like to express his thanks to the National Science Foundation for financial support of the work.

Zusammenfassung—Adenin und Adenosin lassen sich aus wäßriger Lösung bei pH 4·7 polarographisch an der Quecksilbertropfelektrode (DME) beim selben Halbstufenpotential reduzieren. An einer Elektrode aus Pyrolysegraphit (PGE) sind beide voltammetrisch oxidierbar, Adenosin jedoch bei höherem Potential. Die konkurrierende Adsorption beider Verbindungen an der PGE führt dazu, daß der Adeninpeak beim Registrieren der voltammetrischen Oxidation in Gegenwart von Adenosin kleiner wird und bei einer Adenosinkonzentration über 6 m*M* einen konstanten Wert erreicht. In Gemischen wird die Summe beider Verbindungen durch Polarographie an der DME erhalten. Dann wird festes Adenosin zur Lösung gegeben und Adenin durch Voltammetrie an der PGE bestimmt.

Résumé—L'adénine et l'adénosine sont réductibles polarographiquement en solution aqueuse à pH 4,7 à l'électrode à goutte de mercure au même $E_{1/2}$, et sont également oxydables voltammétriquement à l'électrode de toile de platine, mais à des potentiels différents, l'adénosine aux potentiels plus élevés. L'adsorption compétitive des deux composés sur l'électrode de toile de platine a pour conséquence un abaissement dans le pic d'oxydation voltammétrique de l'adénine en la présence d'adénosine, atteignant une valeur constante lorsque la concentration de cette dernière est supérieure à 6 m*M*. Dans les mélanges, la somme des deux est obtenue par polarographie à l'électrode à goutte de mercure. On ajoute alors de l'adénosine solide à la solution et l'on dose l'adénine par voltammétrie a l'électrode de toile de platine.

REFERENCES

1. D. L. Smith and P. J. Elving, *J. Am. Chem. Soc.*, 1962, **84**, 1412.
2. *Idem*, *Anal. Chem.*, 1962, **34**, 930.
3. B. Janik and P. J. Elving, *Chem. Revs.*, 1968, **68**, 295.
4. G. Dryhurst and P. J. Elving, *J. Electrochem. Soc.*, 1968, **115**, 1014.
5. G. Dryhurst, unpublished work.
6. G. Dryhurst and P. J. Elving, *Talanta*, 1969, **16**, 855.
7. B. M. Johnstone and G. P. Briner, *Nature*, 1959, **183**, 681.
8. P. Cerletti and N. Siliprandi, *Ric. Sci.*, 1955, **25**, 208.
9. G. Dryhurst, M. Rosen and P. J. Elving, *Anal. Chim. Acta*, 1968, **42**, 143.
10. G. Dryhurst, *J. Electrochem. Soc.*, 1969, **116**, 1411.
11. R. S. Nicholson and I. Shain, *Anal. Chem.*, 1964, **36**, 706.
12. P. Delahay, *J. Am. Chem. Soc.*, 1953, **75**, 1190.
13. M. Matsuda and Y. Ayabe, *Z. Elektrochem.*, 1955, **59**, 494.
14. R. H. Wopschall and I. Shain, *Anal. Chem.*, 1967, **39**, 1514.
15. B. Breyer and H. H. Bauer, *Alternating Current Polarography and Tensammetry*, Interscience New York, 1963.
16. D. E. Smith and W. H. Reinmuth, *Anal. Chem.*, 1960, **32**, 1892.
17. A. J. Juliard, *J. Electroanal. Chem.*, 1959, **1**, 101.
18. W. L. Underkofler and I. Shain, *Anal. Chem.*, 1965, **37**, 218.
19. D. N. Walker, R. N. Adams and A. L. Juliard, *ibid.*, 1960, **32**, 1526.
20. H. H. Bauer, M. S. Spritzer and P. J. Elving, *J. Electroanal. Chem.*, 1968, **17**, 299.
21. P. Delahay and I. Trachtenberg, *J. Am. Chem. Soc.*, 1957, **79**, 2355.

Talanta, 1972, Vol. 19, pp. 779 to 786. Pergamon Press. Printed in Northern Ireland

SIMULTANEOUS DETERMINATION OF OXYGEN AND NITROGEN IN IRON AND STEEL BY SPARK-SOURCE MASS SPECTROGRAPHY

SHOHEI ODA, ZENJI OHASHI, KEIICHI FURUYA and HITOSHI KAMADA
Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Bunkyo-ku, Tokyo, Japan

(*Received* 19 *May* 1971. *Revised* 14 *October* 1971. *Accepted* 2 *November* 1971)

Summary—A conventional technique has been developed for the simultaneous determination of oxygen and nitrogen in iron and steel by spark-source mass spectrography in the range of 2–400 ppm with a precision of 20%. The instrumental background can be reduced by cryosorption pumping and sample cooling. The adsorbed oxygen on the surface of the sample is easily eliminated by presparking to exhaust the surface concerned. A difference in matrix effect in oxygen determination was observed between iron and steel.

IT IS WELL KNOWN that nitrogen and oxygen in metallic materials seriously affect the mechanical properties. These elements have been determined by vacuum fusion, inert gas fusion, isotope dilution, emission spectrometry and chemical methods.

The use of spark-source mass spectrography for low-level impurity analysis of metals has several advantages over other methods, as has been already established.[1,2] The analysis for non-metallic impurities such as nitrogen and oxygen is, however, still difficult on account of the high instrumental background, and surface contamination of the sample.

Vidal *et al.*[3] tested three different methods for the elimination of adsorbed gases on the surface of iron samples and concluded that the oxygen adsorbed should be removed by eight hours' baking at 150°, but they did not report any oxygen determinations.

Harrington *et al.*[4] discuss the simultaneous determination of carbon, nitrogen and oxygen in metals, with a reduction in the blank by use of a strong cryosorption pump in the source chamber. They concluded that baking the surface surrounding the sparking area did not reduce the intensities of these elements.

Leipziger *et al.*[5] reduced the blank levels for hydrogen, nitrogen and oxygen by baking, presparking, and the judicious choice of etching reagents, to determine levels of 0·1 ppm in gold and platinum. From our experience these samples are not so active towards these elements. With iron samples these authors got only scattered oxygen values, at the 100-ppm level.

A cryosorption pump designed by us gave low instrumental background for nitrogen, but not for oxygen. This effect may be due to contamination on the surface of the sample for sparking.

The method reported here allows the simultaneous determination of nitrogen and oxygen in iron and steel, in the range of 2–400 ppm, with a precision of 20%, using a cryosorption pump in the source chamber and presparking for the elimination of surface contamination of sample.

EXPERIMENTAL

Apparatus and emulsion

A Mattach-Herzog type double-focusing mass spectrograph (Type JMS-01BM, JEOLCO) was used. The chambers of the electrostatic and magnetic analysers were evacuated to a pressure of less than 10^{-8} mmHg. The objective slitwidth was 25 μm to resolve the close proximities of $^{56}Fe^{4+}$ to $^{14}N^{+}$, and $^{32}S^{2+}$ to $^{16}O^{+}$.

Ilford Q2 photographic plates were used. The spectrum line intensity was recorded with a microphotometer (Type JA-2310, Jarrell-Ash Co.).

Quantitative calculation

Although Owens[6] proposed a rapid calibration method, a simplified method was applied. From the spectra of a series of standard samples in which the nitrogen and oxygen contents were already known by other methods, the arbitrary concentration of these elements was calculated with the conventional method on the assumption that their sensitivity and spectrum areas were unity. The ratios of relative sensitivity to spectrum area (S/A) for each elements were determined from the ratios of calculated values *vs.* standard analytical values. The analytical values of unknown samples were calculated from the arbitrary mass spectrographic content and the S/A value thus determined.

Reference analysis

The procedures of the other methods used for the standard samples are reported elsewhere.

Oxygen, vacuum fusion analysis. The conventional analysis at 1650° was used for the determination of oxygen in electrolytic iron and steel. Pure electrolytic iron (15 g) was used as bath metal. For the determination of oxygen in zone-melted iron, the oxygen contamination on the surface of samples was removed by electrolytic polishing and reduction with hydrogen on the surface before analysis.[7]

Nitrogen, isotope dilution analysis. Synthesized ^{15}N-enriched silicon nitride was used as master alloy. A sample (10 g) was sealed into an degassed graphite capsule with a known quantity of the labelled silicon nitride and dropped into a crucible at 1650°. The extracted gas was circulated in the furnace to establish equilibrium. The content of nitrogen-15 was measured by mass spectrometer.[8,9]

Nitrogen, chemical analysis. The conventional Japanese Industrial Standard method (Kjeldahl method) was used.

Reduction of instrumental background and sample preparation

The largest difficulty in mass spectrographic determination of nitrogen and oxgyen in metals is the high instrumental background, and contamination of the sample surface. It was already known by us that it is possible to determine nitrogen as low as several ppm without any special treatment. For oxygen, however, these interferences are intrinsic.

After several trials, presparking of sample electrodes was found to reduce substantially and minimize the effect of adsorbed oxygen on the surface of samples.

A sample was machined into a pair of 15 × 1 × 1 mm electrodes, which were rinsed in dichloroethane and in ethanol with aid of an ultrasonic cleaner. After drying, the sample was set in the electrode holders in the source chamber, and baked for 30 min at 100–150° with an electric heater under a pressure of less than 10^{-6} mmHg. Then the top 2-mm portion of the electrodes was manipulated so as to be exhausted to about 0·1 mm depth, with sparking to clean the surface.

In order to reduce the instrumental background, cryosorption pumping was used as the most convenient method.[4,10] A pumping unit with a 150 × 35 × 1 mm copper support bound with activated charcoal was mounted between the accelerating slit and the earth slit in the source chamber. The unit was kept cool by copper cooling tubes of 12 mm bore which were connected to a liquid nitrogen reservoir. Sample holders were also kept cool by heat conduction through beryllia insulators in contact with other copper cooling tubes.

Figure 1 shows the effects of cryosorption pumping and sample cooling to reduce the instrumental background effect in nitrogen and oxygen determination. The vertical axis in Fig. 1 shows the ratios of ion intensity of nitrogen or oxygen to that of iron. The sample used here was zone-melted iron which contained 6·0 ppm nitrogen and 3·5 ppm oxygen. Figure 1 shows that not only cryosorption pumping but also sample cooling can effectively reduce the oxygen background. It is assumed that the effect of sample cooling is due to a cryosorptive effect rather than to the sample itself. Nitrogen intensities were not changed; no special treatment is required for the determination of nitrogen at the ppm level.

Sparking conditions

The effect of sparking conditions on the intensities of spectrum lines of nitrogen, oxygen and iron was investigated. Figures 2–5 show the results. The sample used was electrolytic iron which contained 200 ppm nitrogen and 300 ppm oxygen. Exposure was 3 × 10^{-11} coulomb. Each point in these figures shows the mean of three determinations. In Fig. 3, min, med, and max show the minimum, mean, and maximum gaps at which the sparks can be struck. As the spectrum intensities of both elements reduce when the gap becomes narrow, the gap was always kept wider than the medium

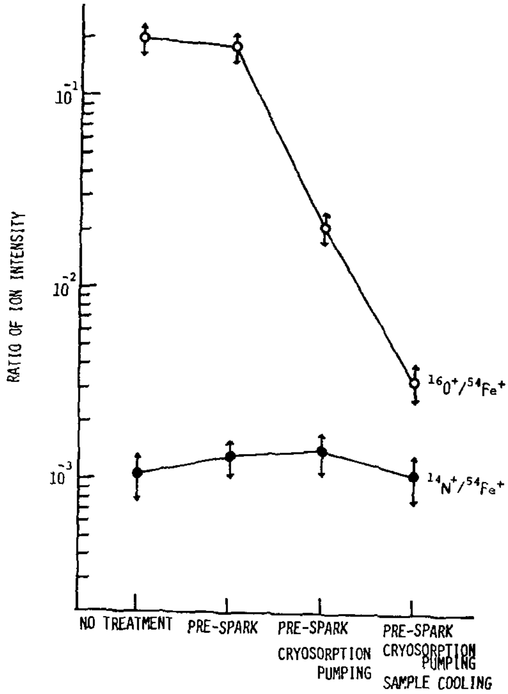


FIG 1.—Effect of cryosorption pumping and sample cooling.

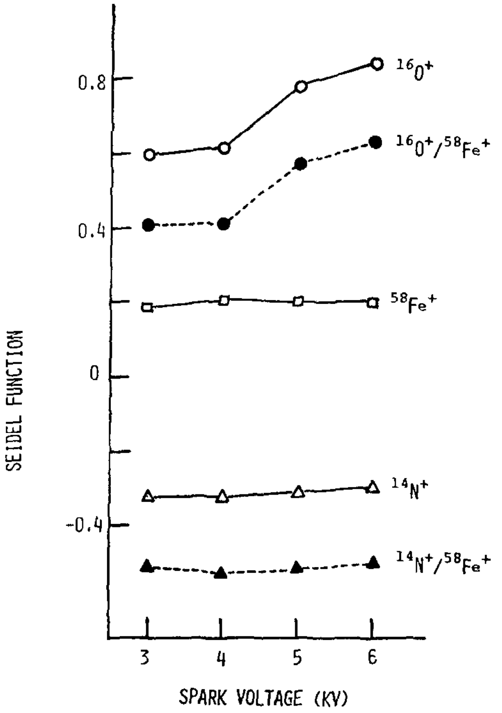


FIG. 2.—Effect of spark voltage.
Pulse duration 40 μsec.
Repetition frequency 100 c/s.
Electrode gap MED.

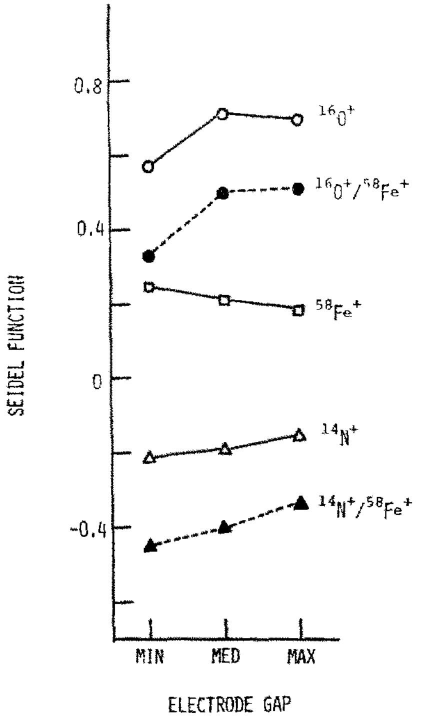


FIG. 3.—Effect of electrode gap.
Spark voltage 5 kV.
Pulse duration 40 μsec.
Repetition frequency 100 c/s.

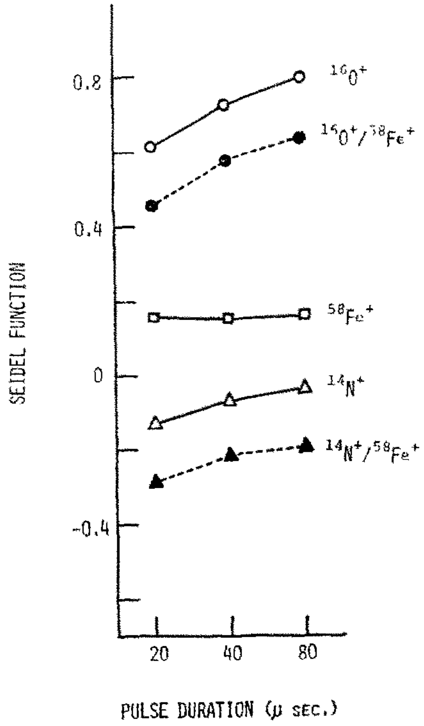


FIG. 4.—Effect of pulse duration.
Spark voltage 5 kV.
Repetition frequency 100 c/s.
Electrode gap MED.

position. Pulse duration, sparking voltage, and electrode gap have large influences on the intensities of spectra. These factors, especially the electrode gap which cannot be controlled instrumentally, should be kept constant throughout the experiment. The adjustment of exposure time was accomplished by change of the repetition frequency, which has the least effect on the line intensity.

The fixed experimental conditions are shown in Table I.

RESULTS

A calibration curve of *S*/*A* for nitrogen and oxygen is shown in Fig. 6. The standard samples consisted of a series of carbon steels (C 0·1–0·8%) and a series of

TABLE I.—EXPERIMENTAL CONDITIONS

Cryosorption pumping and sample cooling	45 min
Instrumental parameters	Objective slitwidth 25 μm Accelerating voltage 25·0 kV Electrostatic voltage 2·5 kV Magnet current 3·0 A (*m*/*e* 3–110)
Sparking conditions	Sparking voltage 5·0 kV (initial; final about 60 kV) Pulse duration 40 μsec Repetition frequency 10, 30, 100, 300, 1000 c/s.
Exposure	3×10^{-13}–3×10^{-9} coulomb (9 stages)
Developing conditions	Developer ID-19, 20°, 4 min Stopping in running water, 30 sec Fixing in Fuji fixer, 3 min Washing in running water, 5 min Drying in hot air, 3–5 min

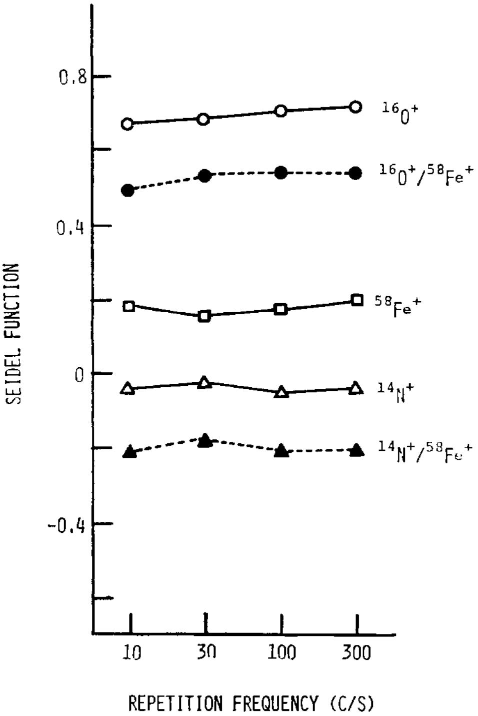


FIG. 5.—Effect of repetition frequency.
Spark voltage 5 kV.
Pulse duration 40 μsec.
Electrode gap MED.

irons. The iron series consisted of four samples of electrolytic iron treated to avoid segmentation effects, and one sample of sintered iron manufactured by Sumitomo Tokushu Kinzoku Co. (Osaka, Japan), from pure iron and alumina powder as a standard sample for gas analysis in vacuum fusion, activation, and other methods.

It is very interesting that there is a remarkable difference in the values of S/A for oxygen in Fig. 6: 4·60 for iron, and 2·35 for steel. It shows there is a difference in the relative sensitivities for oxygen in iron and steel, as the relative area of a spectrum of an element is always constant. On the other hand, in the case of nitrogen no difference can be observed between iron and steel. The relative intensity of the nitrogen spectrum is 1·37.

The necessity of using standard samples in spark-source mass spectrographic determination is often underestimated, and it is recommended for accurate determination that the relative sensitivities of samples are measured by using a series of standards having similar composition to the samples.

The effect of sample cooling was to give a slight reduction of S/A in the nitrogen analysis. The value of S/A without cooling was 1·67, and with cooling it was 1·37.

Table II shows the results of simultaneous determination of nitrogen and oxygen for two types of iron and one type of steel, using values of S/A obtained from Fig. 6.

The precision of the analytical values is about 20% relative standard deviation, and the results were in good agreement with those obtained by other methods. This

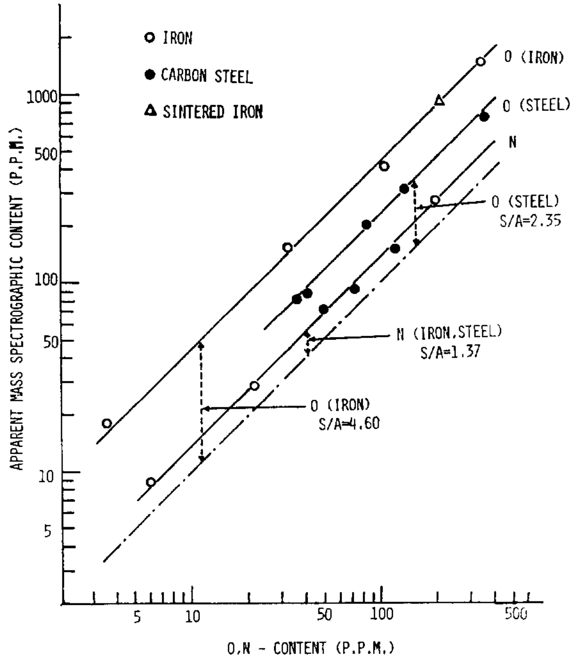


FIG. 6.—Analytical curves.

TABLE II.—ANALYTICAL RESULTS

Sample	Element	Content, *ppm*	Relative standard deviation, %	No. of tests	Values by other methods
Zone-melted iron	O	3·9 ± 0·6	15·4	3	3·5 (V)
	N	6·5 ± 1·6	24·6	3	6·0 (I)
Electrolytic iron	O	320 ± 39	12·2	5	335 (V)
	N	20·7 ± 2·5	12·1	5	21 (I)
Carbon steel (Al-killed)	O	133 ± 30	22·8	5	130 (V)
	N	68·2 ± 14	20·2	5	72 (K)

(V), Vacuum fusion; (I), isotope dilution; (K), Kjeldahl.

procedure can be applied to practical samples in the range of 2–400 ppm oxygen or nitrogen. Although the detection limits of this method have not been discussed, because of the lack of standard samples which contain less nitrogen and oxygen than those used in this experiment, it may be considered as 1 ppm from the results of other experiments in which the instrumental background was found to be less than 1 ppm when high-purity silicon electrodes were used.

DISCUSSION

It is commonly assumed that almost all elements have nearly equal sensitivities and that the sensitivity of an element is not influenced by the other elements present. It is, however, very interesting that a large difference in relative sensitivities was observed for oxygen in iron and steel. This phenomenon has never been reported, and it will be discussed here briefly.

As the sparking mechanism in the mass spectrographic analysis is very complex and might be a combination of several ionization mechanisms, it is still very hard to discuss the mechanism on the basis of the limited results obtained. More experimental data on the mechanism are needed, obtained by using time-resolving and other techniques. Possible reasons for the difference in sensitivity of oxygen are as follows. (1) Difference of the state of oxygen in iron and steel. Oxygen in iron exists in the form of FeO or dissolved oxygen, whereas in steel most oxygen exists as more stable oxides, *e.g.*, Al_2O_3, SiO_2. A difference in vaporization and dissociation energies between these oxides may bring about the difference of ionization efficiency of oxygen. (2) Other elements existing in steel may reduce the relative sensitivity of oxygen. Some elements which have low ionization potential may reduce the ionization yield of oxygen which has relatively high ionization potential, and the other elements may recombine with oxygen extracted from sample electrodes, and so reduce the yield. (3) Sample cooling may promote selective distillation and so reduce the ionization yield of oxygen.

Of these reasons, (1) should be discarded, as the oxygen sensitivity of the sintered iron in which the oxygen exists as alumina, has the same value as that of the electrolytic iron; (3) is considered to be unlikely on present knowledge. The second reason is assumed to be most likely, because steel contains so many alloying elements.

The dependence of the spectrum intensity on the electrode gap may be explained on the assumption that the local spark-breaking voltage is dependent on the length of gap. This is supported by the curves in Fig. 2; the higher the sparking voltage, the stronger the intensities of both elements. As a possible improvement for analytical precision, it is recommended that a voltage control element be built in the spark source circuit, thus achieving independence between the spark-breaking voltage and the electrode gap.

The dependence of spectrum intensities on other conditions such as sparking voltage and pulse duration will also cause significant analytical errors.

From these considerations, it can be said that the relative sensitivity of an element not only depends on the kind of element, but also on the experimental conditions, matrix elements, and other constituents. For an accurate mass spectrographic measurement, it is best to obtain the relative sensitivities by using a series of standards which have similar composition to the sample.

Zusammenfassung—Ein schon bekanntes Verfahren wurde für die gleichzeitige Bestimmung von Sauerstoff und Stickstoff in Eisen und Stahl weiterentwickelt. Man verwendet ein Massenspektrometer mit Funkenquelle und kann damit im Bereich 2–400 ppm eine Genauigkeit von 20% erzielen. Der Untergrund des Instruments kann durch Kryosorptionspumpen und Kühlung der Probe reduziert werden. Der an der Probenoberfläche adsorbierte Sauerstoff kann leicht durch vorheriges Abfunken beseitigt werden; dadurch wird die betreffende Oberfläche gereinigt. Bei der Sauerstoffbestimmung wurde zwischen Eisen und Stahl ein Unterschied im Matrixeffekt gefunden.

Résumé—On a élaboré une technique ordinaire pour le dosage simultané de l'oxygène et de l'azote dans le fer et l'acier par spectrographie de masse à source d'étincelle, dans le domaine de 2–400 ppm, avec une précision de 20%. On peut réduire le fond instrumental par pompage

en cryosorption et refroidissement de l'échantillon. On élimine aisément l'oxygène adsorbé sur la surface de l'échantillon par jaillissement préalable d'étincelle pour épuiser la surface concernèe. On a observé une différence d'effet de matrice dans la détermination de l'oxygène entre le fer et l'acier.

LITERATURE

1. R. D. Caraig, G. A. Errock and J. P. Waldron, *Advances in Mass Spectrometry*, J. P. Waldron, Ed., p. 136. Pergamon, London, 1959.
2. J. Kai, *Shitsuryo Bunseki*, 1963, **11**, 37.
3. G. Vidal, P. Galmard and P. Lanusse, *Anal. Chem.*, 1970, **42**, 98.
4. W. L. Harrington, R. K. Skogerboe and G. H. Morrison, *ibid.*, 1966, **38**, 821.
5. F. D. Leipziger and R. J. Guidoboni, *Appl. Spectry.*, 1967, **21**, 165.
6. E. B. Owens and N. A. Giardino, *Anal. Chem.*, 1963, **35**, 1172.
7. K. Furuya, T. Kikuchi and H. Kamada, *Bunseki Kagaku*, 1968, **17**, 770.
8. K. Furuya, S. Okuyama, S. Tachikawa and H. Kamada, *Talanta*, 1968, **15**, 327.
9. K. Furuya and T. Kikuchi, *Bunseki Kagaku*, in the press.
10. W. L. Harrington, R. K. Skogerboe and G. H. Morrison, *Anal. Chem.*, 1965, **37**, 1480.

Talanta, 1972, Vol. 19, pp. 779 to 786. Pergamon Press. Printed in Northern Ireland

SIMULTANEOUS DETERMINATION OF OXYGEN AND NITROGEN IN IRON AND STEEL BY SPARK-SOURCE MASS SPECTROGRAPHY

SHOHEI ODA, ZENJI OHASHI, KEIICHI FURUYA and HITOSHI KAMADA
Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Bunkyo-ku, Tokyo, Japan

(*Received* 19 *May* 1971. *Revised* 14 *October* 1971. *Accepted* 2 *November* 1971)

Summary—A conventional technique has been developed for the simultaneous determination of oxygen and nitrogen in iron and steel by spark-source mass spectrography in the range of 2–400 ppm with a precision of 20%. The instrumental background can be reduced by cryosorption pumping and sample cooling. The adsorbed oxygen on the surface of the sample is easily eliminated by presparking to exhaust the surface concerned. A difference in matrix effect in oxygen determination was observed between iron and steel.

IT IS WELL KNOWN that nitrogen and oxygen in metallic materials seriously affect the mechanical properties. These elements have been determined by vacuum fusion, inert gas fusion, isotope dilution, emission spectrometry and chemical methods.

The use of spark-source mass spectrography for low-level impurity analysis of metals has several advantages over other methods, as has been already established.[1,2] The analysis for non-metallic impurities such as nitrogen and oxygen is, however, still difficult on account of the high instrumental background, and surface contamination of the sample.

Vidal *et al.*[3] tested three different methods for the elimination of adsorbed gases on the surface of iron samples and concluded that the oxygen adsorbed should be removed by eight hours' baking at 150°, but they did not report any oxygen determinations.

Harrington *et al.*[4] discuss the simultaneous determination of carbon, nitrogen and oxygen in metals, with a reduction in the blank by use of a strong cryosorption pump in the source chamber. They concluded that baking the surface surrounding the sparking area did not reduce the intensities of these elements.

Leipziger *et al.*[5] reduced the blank levels for hydrogen, nitrogen and oxygen by baking, presparking, and the judicious choice of etching reagents, to determine levels of 0·1 ppm in gold and platinum. From our experience these samples are not so active towards these elements. With iron samples these authors got only scattered oxygen values, at the 100-ppm level.

A cryosorption pump designed by us gave low instrumental background for nitrogen, but not for oxygen. This effect may be due to contamination on the surface of the sample for sparking.

The method reported here allows the simultaneous determination of nitrogen and oxygen in iron and steel, in the range of 2–400 ppm, with a precision of 20%, using a cryosorption pump in the source chamber and presparking for the elimination of surface contamination of sample.

EXPERIMENTAL

Apparatus and emulsion

A Mattach-Herzog type double-focusing mass spectrograph (Type JMS-01BM, JEOLCO) was used. The chambers of the electrostatic and magnetic analysers were evacuated to a pressure of less than 10^{-8} mmHg. The objective slitwidth was 25 μm to resolve the close proximities of $^{56}Fe^{4+}$ to $^{14}N^{+}$, and $^{32}S^{2+}$ to $^{16}O^{+}$.

Ilford Q2 photographic plates were used. The spectrum line intensity was recorded with a microphotometer (Type JA-2310, Jarrell-Ash Co.).

Quantitative calculation

Although Owens[6] proposed a rapid calibration method, a simplified method was applied. From the spectra of a series of standard samples in which the nitrogen and oxygen contents were already known by other methods, the arbitrary concentration of these elements was calculated with the conventional method on the assumption that their sensitivity and spectrum areas were unity. The ratios of relative sensitivity to spectrum area (S/A) for each elements were determined from the ratios of calculated values *vs.* standard analytical values. The analytical values of unknown samples were calculated from the arbitrary mass spectrographic content and the S/A value thus determined.

Reference analysis

The procedures of the other methods used for the standard samples are reported elsewhere.

Oxygen, vacuum fusion analysis. The conventional analysis at 1650° was used for the determination of oxygen in electrolytic iron and steel. Pure electrolytic iron (15 g) was used as bath metal. For the determination of oxygen in zone-melted iron, the oxygen contamination on the surface of samples was removed by electrolytic polishing and reduction with hydrogen on the surface before analysis.[7]

Nitrogen, isotope dilution analysis. Synthesized ^{15}N-enriched silicon nitride was used as master alloy. A sample (10 g) was sealed into an degassed graphite capsule with a known quantity of the labelled silicon nitride and dropped into a crucible at 1650°. The extracted gas was circulated in the furnace to establish equilibrium. The content of nitrogen-15 was measured by mass spectrometer.[8,9]

Nitrogen, chemical analysis. The conventional Japanese Industrial Standard method (Kjeldahl method) was used.

Reduction of instrumental background and sample preparation

The largest difficulty in mass spectrographic determination of nitrogen and oxgyen in metals is the high instrumental background, and contamination of the sample surface. It was already known by us that it is possible to determine nitrogen as low as several ppm without any special treatment. For oxygen, however, these interferences are intrinsic.

After several trials, presparking of sample electrodes was found to reduce substantially and minimize the effect of adsorbed oxygen on the surface of samples.

A sample was machined into a pair of 15 × 1 × 1 mm electrodes, which were rinsed in dichloroethane and in ethanol with aid of an ultrasonic cleaner. After drying, the sample was set in the electrode holders in the source chamber, and baked for 30 min at 100–150° with an electric heater under a pressure of less than 10^{-6} mmHg. Then the top 2-mm portion of the electrodes was manipulated so as to be exhausted to about 0·1 mm depth, with sparking to clean the surface.

In order to reduce the instrumental background, cryosorption pumping was used as the most convenient method.[4,10] A pumping unit with a 150 × 35 × 1 mm copper support bound with activated charcoal was mounted between the accelerating slit and the earth slit in the source chamber. The unit was kept cool by copper cooling tubes of 12 mm bore which were connected to a liquid nitrogen reservoir. Sample holders were also kept cool by heat conduction through beryllia insulators in contact with other copper cooling tubes.

Figure 1 shows the effects of cryosorption pumping and sample cooling to reduce the instrumental background effect in nitrogen and oxygen determination. The vertical axis in Fig. 1 shows the ratios of ion intensity of nitrogen or oxygen to that of iron. The sample used here was zone-melted iron which contained 6·0 ppm nitrogen and 3·5 ppm oxygen. Figure 1 shows that not only cryosorption pumping but also sample cooling can effectively reduce the oxygen background. It is assumed that the effect of sample cooling is due to a cryosorptive effect rather than to the sample itself. Nitrogen intensities were not changed; no special treatment is required for the determination of nitrogen at the ppm level.

Sparking conditions

The effect of sparking conditions on the intensities of spectrum lines of nitrogen, oxygen and iron was investigated. Figures 2–5 show the results. The sample used was electrolytic iron which contained 200 ppm nitrogen and 300 ppm oxygen. Exposure was 3 × 10^{-11} coulomb. Each point in these figures shows the mean of three determinations. In Fig. 3, min, med, and max show the minimum, mean, and maximum gaps at which the sparks can be struck. As the spectrum intensities of both elements reduce when the gap becomes narrow, the gap was always kept wider than the medium

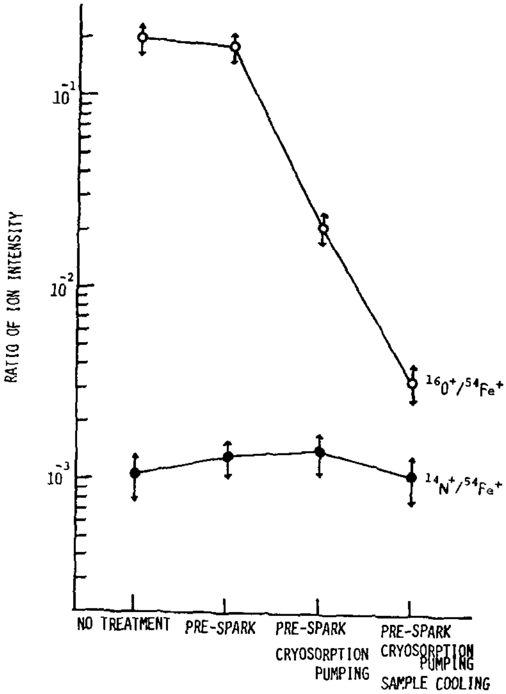


FIG 1.—Effect of cryosorption pumping and sample cooling.

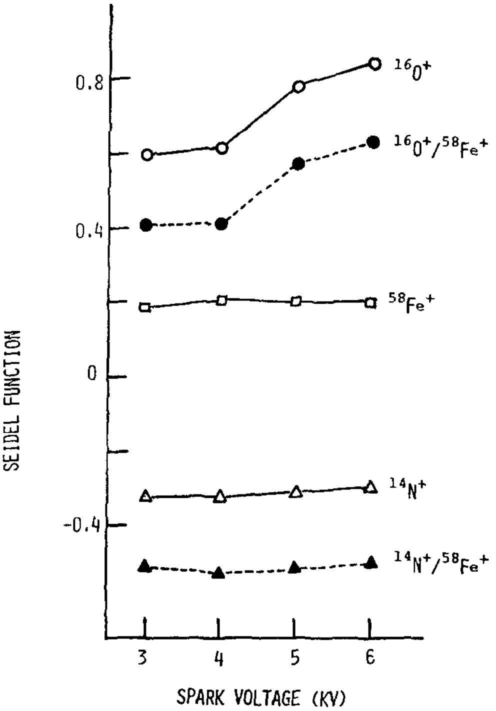


FIG. 2.—Effect of spark voltage.
Pulse duration 40 μsec.
Repetition frequency 100 c/s.
Electrode gap MED.

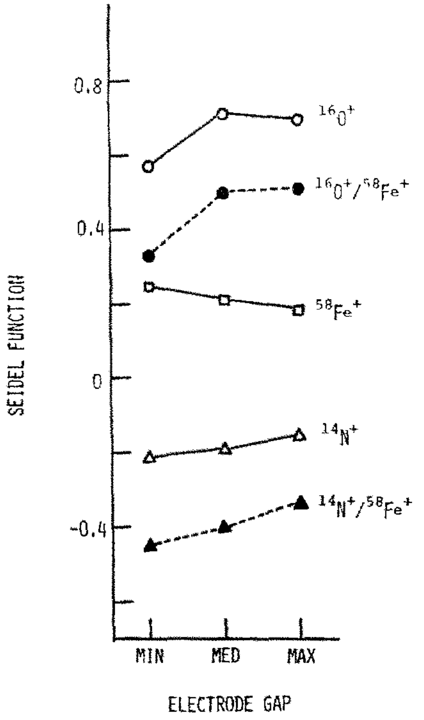


FIG. 3.—Effect of electrode gap.
Spark voltage 5 kV.
Pulse duration 40 μsec.
Repetition frequency 100 c/s.

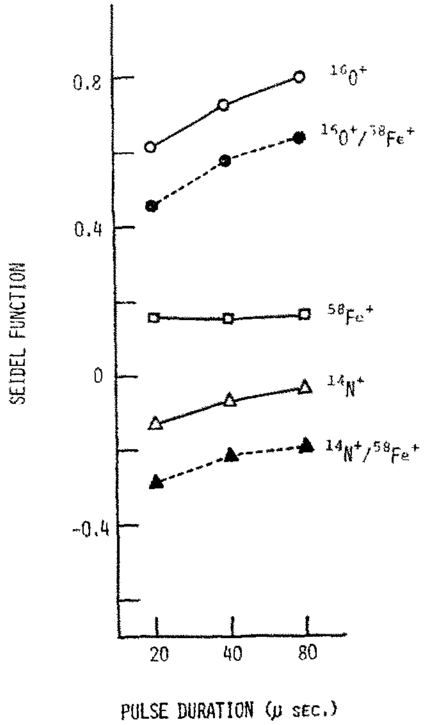


FIG. 4.—Effect of pulse duration.
Spark voltage 5 kV.
Repetition frequency 100 c/s.
Electrode gap MED.

position. Pulse duration, sparking voltage, and electrode gap have large influences on the intensities of spectra. These factors, especially the electrode gap which cannot be controlled instrumentally, should be kept constant throughout the experiment. The adjustment of exposure time was accomplished by change of the repetition frequency, which has the least effect on the line intensity.

The fixed experimental conditions are shown in Table I.

RESULTS

A calibration curve of S/A for nitrogen and oxygen is shown in Fig. 6. The standard samples consisted of a series of carbon steels (C 0·1–0·8 %) and a series of

TABLE I.—EXPERIMENTAL CONDITIONS

Cryosorption pumping and sample cooling	45 min
Instrumental parameters	Objective slitwidth 25 μm
	Accelerating voltage 25·0 kV
	Electrostatic voltage 2·5 kV
	Magnet current 3·0 A (m/e 3–110)
Sparking conditions	Sparking voltage 5·0 kV (initial; final about 60 kV)
	Pulse duration 40 μsec
	Repetition frequency 10, 30, 100, 300, 1000 c/s.
Exposure	3×10^{-13}–3×10^{-9} coulomb (9 stages)
Developing conditions	Developer ID-19, 20°, 4 min
	Stopping in running water, 30 sec
	Fixing in Fuji fixer, 3 min
	Washing in running water, 5 min
	Drying in hot air, 3–5 min

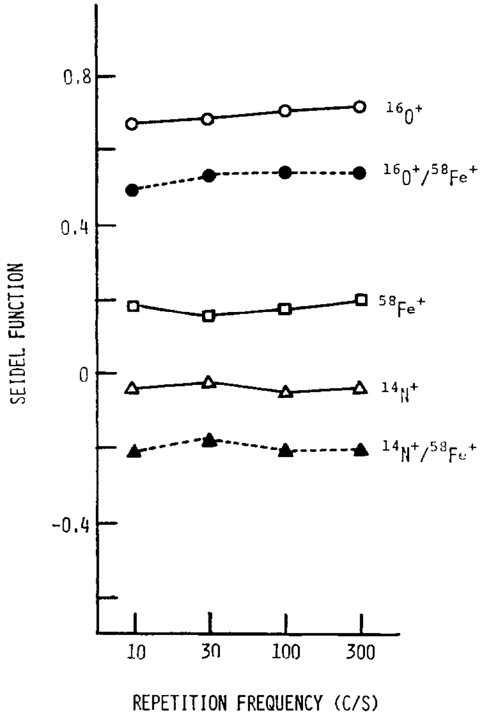


FIG. 5.—Effect of repetition frequency.
Spark voltage 5 kV.
Pulse duration 40 μsec.
Electrode gap MED.

irons. The iron series consisted of four samples of electrolytic iron treated to avoid segmentation effects, and one sample of sintered iron manufactured by Sumitomo Tokushu Kinzoku Co. (Osaka, Japan), from pure iron and alumina powder as a standard sample for gas analysis in vacuum fusion, activation, and other methods.

It is very interesting that there is a remarkable difference in the values of *S*/*A* for oxygen in Fig. 6: 4·60 for iron, and 2·35 for steel. It shows there is a difference in the relative sensitivities for oxygen in iron and steel, as the relative area of a spectrum of an element is always constant. On the other hand, in the case of nitrogen no difference can be observed between iron and steel. The relative intensity of the nitrogen spectrum is 1·37.

The necessity of using standard samples in spark-source mass spectrographic determination is often underestimated, and it is recommended for accurate determination that the relative sensitivities of samples are measured by using a series of standards having similar composition to the samples.

The effect of sample cooling was to give a slight reduction of *S*/*A* in the nitrogen analysis. The value of *S*/*A* without cooling was 1·67, and with cooling it was 1·37.

Table II shows the results of simultaneous determination of nitrogen and oxygen for two types of iron and one type of steel, using values of *S*/*A* obtained from Fig. 6.

The precision of the analytical values is about 20% relative standard deviation, and the results were in good agreement with those obtained by other methods. This

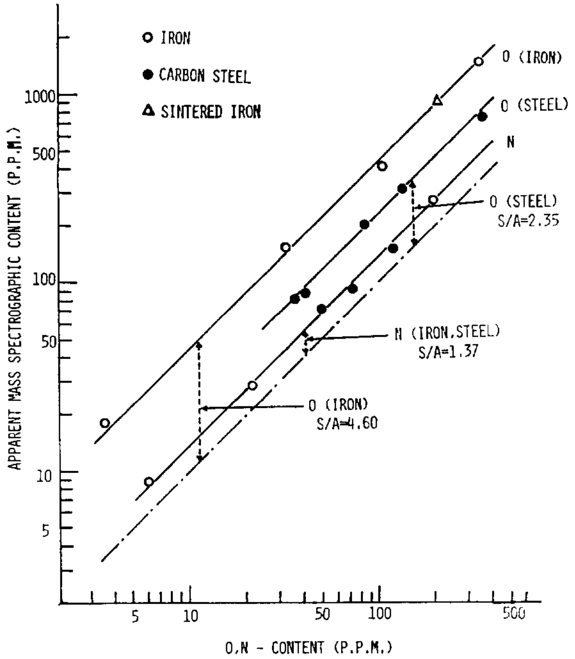


FIG. 6.—Analytical curves.

TABLE II.—ANALYTICAL RESULTS

Sample	Element	Content, *ppm*	Relative standard deviation, %	No. of tests	Values by other methods
Zone-melted iron	O	3·9 ± 0·6	15·4	3	3·5 (V)
	N	6·5 ± 1·6	24·6	3	6·0 (I)
Electrolytic iron	O	320 ± 39	12·2	5	335 (V)
	N	20·7 ± 2·5	12·1	5	21 (I)
Carbon steel (Al-killed)	O	133 ± 30	22·8	5	130 (V)
	N	68·2 ± 14	20·2	5	72 (K)

(V), Vacuum fusion; (I), isotope dilution; (K), Kjeldahl.

procedure can be applied to practical samples in the range of 2–400 ppm oxygen or nitrogen. Although the detection limits of this method have not been discussed, because of the lack of standard samples which contain less nitrogen and oxygen than those used in this experiment, it may be considered as 1 ppm from the results of other experiments in which the instrumental background was found to be less than 1 ppm when high-purity silicon electrodes were used.

DISCUSSION

It is commonly assumed that almost all elements have nearly equal sensitivities and that the sensitivity of an element is not influenced by the other elements present. It is, however, very interesting that a large difference in relative sensitivities was observed for oxygen in iron and steel. This phenomenon has never been reported, and it will be discussed here briefly.

As the sparking mechanism in the mass spectrographic analysis is very complex and might be a combination of several ionization mechanisms, it is still very hard to discuss the mechanism on the basis of the limited results obtained. More experimental data on the mechanism are needed, obtained by using time-resolving and other techniques. Possible reasons for the difference in sensitivity of oxygen are as follows. (1) Difference of the state of oxygen in iron and steel. Oxygen in iron exists in the form of FeO or dissolved oxygen, whereas in steel most oxygen exists as more stable oxides, *e.g.*, Al_2O_3, SiO_2. A difference in vaporization and dissociation energies between these oxides may bring about the difference of ionization efficiency of oxygen. (2) Other elements existing in steel may reduce the relative sensitivity of oxygen. Some elements which have low ionization potential may reduce the ionization yield of oxygen which has relatively high ionization potential, and the other elements may recombine with oxygen extracted from sample electrodes, and so reduce the yield. (3) Sample cooling may promote selective distillation and so reduce the ionization yield of oxygen.

Of these reasons, (1) should be discarded, as the oxygen sensitivity of the sintered iron in which the oxygen exists as alumina, has the same value as that of the electrolytic iron; (3) is considered to be unlikely on present knowledge. The second reason is assumed to be most likely, because steel contains so many alloying elements.

The dependence of the spectrum intensity on the electrode gap may be explained on the assumption that the local spark-breaking voltage is dependent on the length of gap. This is supported by the curves in Fig. 2; the higher the sparking voltage, the stronger the intensities of both elements. As a possible improvement for analytical precision, it is recommended that a voltage control element be built in the spark source circuit, thus achieving independence between the spark-breaking voltage and the electrode gap.

The dependence of spectrum intensities on other conditions such as sparking voltage and pulse duration will also cause significant analytical errors.

From these considerations, it can be said that the relative sensitivity of an element not only depends on the kind of element, but also on the experimental conditions, matrix elements, and other constituents. For an accurate mass spectrographic measurement, it is best to obtain the relative sensitivities by using a series of standards which have similar composition to the sample.

Zusammenfassung—Ein schon bekanntes Verfahren wurde für die gleichzeitige Bestimmung von Sauerstoff und Stickstoff in Eisen und Stahl weiterentwickelt. Man verwendet ein Massenspektrometer mit Funkenquelle und kann damit im Bereich 2–400 ppm eine Genauigkeit von 20% erzielen. Der Untergrund des Instruments kann durch Kryosorptionspumpen und Kühlung der Probe reduziert werden. Der an der Probenoberfläche adsorbierte Sauerstoff kann leicht durch vorheriges Abfunken beseitigt werden; dadurch wird die betreffende Oberfläche gereinigt. Bei der Sauerstoffbestimmung wurde zwischen Eisen und Stahl ein Unterschied im Matrixeffekt gefunden.

Résumé—On a élaboré une technique ordinaire pour le dosage simultané de l'oxygène et de l'azote dans le fer et l'acier par spectrographie de masse à source d'étincelle, dans le domaine de 2–400 ppm, avec une précision de 20%. On peut réduire le fond instrumental par pompage

en cryosorption et refroidissement de l'échantillon. On élimine aisément l'oxygène adsorbé sur la surface de l'échantillon par jaillissement préalable d'étincelle pour épuiser la surface concernèe. On a observé une différence d'effet de matrice dans la détermination de l'oxygène entre le fer et l'acier.

LITERATURE

1. R. D. Caraig, G. A. Errock and J. P. Waldron, *Advances in Mass Spectrometry*, J. P. Waldron, Ed., p. 136. Pergamon, London, 1959.
2. J. Kai, *Shitsuryo Bunseki*, 1963, **11**, 37.
3. G. Vidal, P. Galmard and P. Lanusse, *Anal. Chem.*, 1970, **42**, 98.
4. W. L. Harrington, R. K. Skogerboe and G. H. Morrison, *ibid.*, 1966, **38**, 821.
5. F. D. Leipziger and R. J. Guidoboni, *Appl. Spectry.*, 1967, **21**, 165.
6. E. B. Owens and N. A. Giardino, *Anal. Chem.*, 1963, **35**, 1172.
7. K. Furuya, T. Kikuchi and H. Kamada, *Bunseki Kagaku*, 1968, **17**, 770.
8. K. Furuya, S. Okuyama, S. Tachikawa and H. Kamada, *Talanta*, 1968, **15**, 327.
9. K. Furuya and T. Kikuchi, *Bunseki Kagaku*, in the press.
10. W. L. Harrington, R. K. Skogerboe and G. H. Morrison, *Anal. Chem.*, 1965, **37**, 1480.

Talanta, 1972, Vol. 19, pp. 787 to 790. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Indirect method for the determination of aluminium by atomic-absorption spectrometry using an air–acetylene flame

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

It has been reported that serious interelement interferences are observed in the atomic-absorption determination of iron under certain operating conditions using an air–acetylene flame.[1,2] When flame conditions are optimized for maximum iron absorbance to be obtained for solutions prepared in sulphate or nitrate media, cobalt, nickel and copper cause depressive interferences.[2] Maximum absorption by iron occurs in a slightly fuel-lean air–acetylene flame, but in the stoichiometric or fuel-rich flame the iron absorption falls sharply when a purely sulphate or nitrate medium is used. Under these conditions many metals cause enhancement of the iron absorbance,[3] and of these, titanium, aluminium, calcium and zirconium are notable for the very low concentrations at which they interfere. A similar interference pattern has also been observed for nickel, cobalt and chromium[3,4] and may be explained on the basis of overexcitation phenomena.[3,5]

The enhancement effect has been used to provide a sensitive indirect method for the determination of titanium in the concentration range 0·01–10 ppm.[6] This paper reports a similar method for aluminium and includes a more detailed discussion of the choice of matrix element and the interference effects in this type of procedure. Aluminium cannot normally be determined directly by using an air–acetylene flame[7] as the monoxide AlO is not sufficiently dissociated in this flame,[8] but a working range of 50–500 ppm aluminium has recently been attained in a direct procedure in the presence of ammonium fluoride.[9] Normally either a nitrous oxide–acetylene flame or an oxy-acetylene flame must be used and a detection limit of about 1 ppm may be readily obtained.[7,10,11] Unfortunately, this is not sufficiently sensitive for many routine industrial applications and the method proposed here, which has a limit approximately two orders of magnitude lower than this, may be suitable in some cases.

EXPERIMENTAL

A Perkin–Elmer 290 Atomic Absorption Spectrometer and hollow-cathode lamps were used and operated at the manufacturer's recommended settings. The standard 50-mm slot tubular burner head and the 50-mm slot high-temperature head were used for air–acetylene and nitrous oxide–acetylene flames respectively. Gas flow-rates were measured with Fischer and Porter ¼-in. bore flowmeters and corrected to atmospheric pressure. The air flow-rate was maintained at 46 l./min (equivalent to a flowmeter reading of 14·0 at a feed pressure of 35 psig) and the acetylene flow-rate varied between 2·0 and 4·8 l./min (equivalent to a flowmeter reading of 13·7 at a feed pressure of 8 psig). The optimum height of the optical beam above the burner for maximum enhancement was found to be 15 mm, and absorbance readings were recorded on a Honeywell Electronik 19 chart recorder.

Stock solutions of all the metals in sulphate medium were prepared as described previously.[6] A 1000-ppm aluminium solution was prepared from 1 g of aluminium powder dissolved in sulphuric acid and diluted to 1 litre so that the final concentration of sulphuric acid was $10^{-3}M$. Distilled water from an all-quartz still[12] was used throughout. The purity of water from other types of still was not adequate, presumably because of the effect of very small amounts of calcium on the phenomena to be described. Care must be taken to avoid the addition of chloride ions.

RESULTS AND DISCUSSION

The sharp drop in absorbance by iron (as sulphate or nitrate) which occurs in a fuel-rich air–acetylene flame has been described previously.[3,5] The enhancement effect of small amounts of aluminium on this depression of the iron signal in the fuel-rich flame is shown in Fig. 1. The enhancement for a 25-ppm iron solution gives a linear relationship between 0·25 and 1·2 ppm of aluminium. The signal became more or less constant from 2 up to at least 500 ppm aluminium. The shape and characteristics of this calibration curve and the enhancement effect itself are dependent on the geometry of the burner and optical systems and their orientation relative to one another. This would be

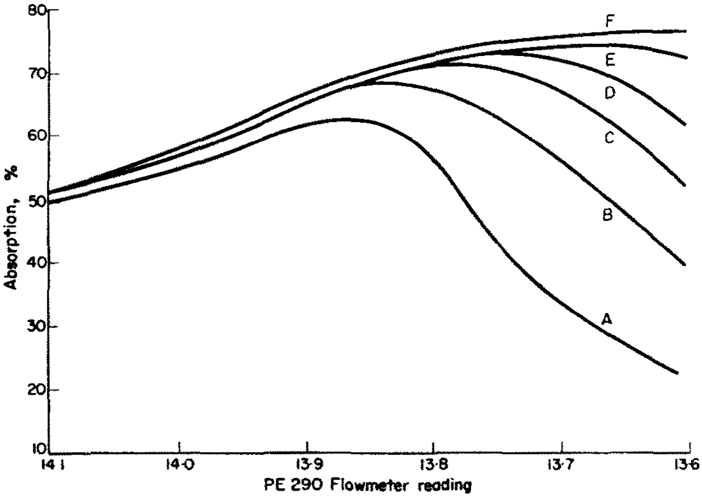


FIG. 1.—Absorption of 25 ppm iron(III) in sulphate medium as a function of acetylene flow-rate. Concentration of aluminium added: (*A*) none; (*B*) 0·5 ppm; (*C*) 1 ppm; (*D*) 2 ppm; (*E*) 10 ppm; (*F*) 500 ppm.

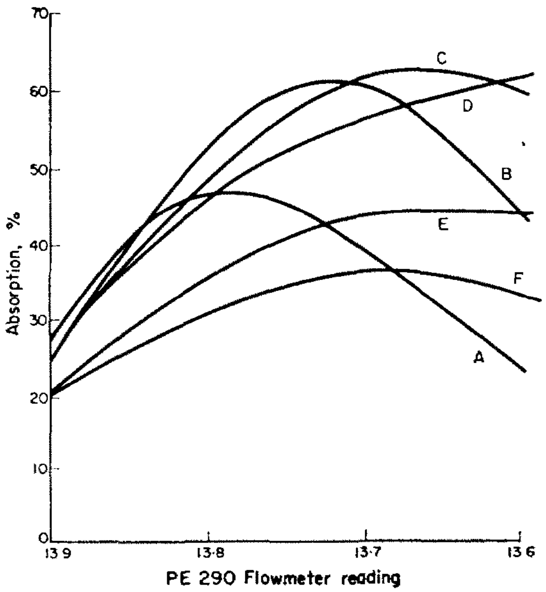


FIG. 2.—Absorption of 10 ppm chromium in sulphate medium as a function of acetylene flow-rate. Concentration of aluminium added: (*A*) none; (*B*) 0·5 ppm; (*C*) 2 ppm; (*D*) 20 ppm; (*E*) 100 ppm; (*F*) 500 ppm.

expected to depend on the particular instrument used but with the PE 290 fitted with a standard air-acetylene burner the optimum conditions for maximum sensitivity are those given above. The working range for the determination of aluminium may be varied by using different concentrations of iron. Thus, for example, the most sensitive conditions with our apparatus required use of 10 ppm of iron when the working range was 0·01–0·09 ppm of aluminium. At higher concentrations of iron, higher levels of aluminium may be detected but concentrations above 25 ppm would mean working in the range in which the direct atomic-absorption determination of aluminium is possible and the method would therefore not be particularly advantageous.

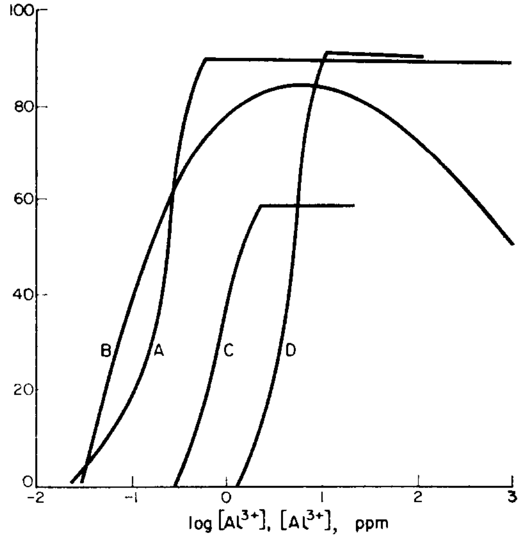


FIG. 3.—Effect of aluminium at a fuel-flow of 13·7 (meter reading) and burner height of 15 mm, on (*A*) 10 ppm of iron; (*B*) 10 ppm of chromium; (*C*) 25 ppm of cobalt; (*D*) 25 ppm of nickel; all in sulphate medium.

Aluminium gives a similar enhancement of the signals of cobalt, nickel and chromium and any of these may be used as the matrix element. The effect for chromium is shown in Fig. 2 and occurs only in the fuel-rich air–acetylene flame. At high aluminium concentrations the chromium signal does not reach a constant level but begins to fall again (Fig. 2), the maximum in the calibration curve depending on the chromium concentration, being at 5 ppm of aluminium for 10 ppm of chromium. The effect of aluminium on the atomic-absorption signals of cobalt and nickel was very similar to that for iron, although the detection of aluminium was far less sensitive with nickel. The effects of increasing aluminium concentration are shown in Fig. 3 for all four elements, which suggests that iron is the most suitable matrix element.

The operating conditions will vary from one instrument to another but they may be summarized as follows. (*i*) Slightly fuel-rich air-acetylene flame such that yellow carbon incandescence is just visible. (*ii*) Light-beam centred at 15–20 mm above the burner head. (*iii*) Matrix element iron(III) sulphate in $10^{-3}M$ sulphuric acid at an iron concentration appropriate to the working range required. (*iv*) Aluminium standards and samples prepared as sulphate and/or nitrate solutions.

We have investigated some interference effects on this procedure and these are largely as expected from the known effects of the elements on the atomic-absorption signal of iron.[8] Elements that behave in a similar manner to aluminium, *e.g.*, calcium and titanium, interfere at an equivalent concentration to the aluminium, whereas others that give an enhancement or depression of the iron signal at concentrations equivalent to the iron concentration, *e.g.*, nickel and chromium, interfere at a similar level. Thus, this method is only suitable for relatively pure aluminium solutions or for analyses in which a separation process is also included. It does, however, offer a substantial improvement in detection limit over that normally obtainable by direct atomic-absorption spectrometry, using either a nitrous oxide–acetylene or oxy-acetylene flame.

Department of Pure and Applied Chemistry
University of Strathclyde
Cathedral Street
Glasgow, C.1. Scotland

J. M. OTTAWAY
D. T. COKER*
B. SINGLETON

Summary—The enhancement of the atomic-absorption signals of iron, cobalt, nickel and chromium in a fuel-rich air–acetylene flame by small amounts of aluminium makes possible the indirect determination of aluminium in the concentration range 0·01–10 ppm. The optimization of working conditions and the occurrence of interferences are reported.

* Present address: Esso Research Centre, Abingdon, Berkshire.

Zusammenfassung—Die Verstärkung der Atomabsorptions-Signale von Eisen, Kobalt, Nickel und Chrom in einer fetten Luft-Acetylen-Flamme durch kleine Mengen Aluminium ermöglicht die indirekte Bestimmung von Aluminium im Konzentrationsbereich 0,01–10 ppm. Es wird über die Optimierung der Arbeitsbedingungen und das Auftreten von Störungen berichtet.

Résumé—Le renforcement des signaux d'absorption atomique des fer, cobalt, nickel et chrome dans une flamme air–acétylène riche en combustible par de petites quantités d'aluminium rend possible le dosage indirect de l'aluminium dans le domaine de concentration 0,01–10 ppm. On décrit l'optimalisation des conditions de travail et la présence d'interférences.

REFERENCES

1. K. E. Curtis, *Analyst*, 1969, **94**, 1068.
2. J. M. Ottaway, D. T. Coker, W. B. Rowston and D. R. Bhattarai, *ibid.*, 1970, **95**, 567.
3. D. T. Coker, *M.Sc. Thesis*, University of Strathclyde, 1970.
4. J. A. Davies, *M.Sc. Thesis*, University of Strathclyde, 1970.
5. D. T. Coker and J. M. Ottaway, *Nature*, 1970, **227**, 831.
6. J. M. Ottaway, D. T. Coker and J. A. Davies, *Anal. Lett.*, 1970, **3**, 385.
7. R. J. Jaworowski, R. P. Weberling and D. J. Bracco, *Anal. Chim. Acta*, 1967, **37**, 284.
8. D. T. Coker and J. M. Ottaway, *Nature*, 1971, **230**, 156.
9. A. Hofer, *Z. Anal. Chem.*, 1971, **253**, 206.
10. M. D. Amos and P. E. Thomas, *Anal. Chim. Acta*, 1965, **32**, 139.
11. T. V. Ramakrishna, P. W. West and J. W. Robinson, *ibid.*, 1967, **39**, 81.
12. E. Bishop and J. R. B. Sutton, *ibid.*, 1960, **22**, 590.

Talanta, 1972, Vol. 19, pp. 790 to 793. Pergamon Press. Printed in Northern Ireland

Precipitation of barium chromate in the presence of strontium and lead by complexation followed by volatilization of ammonia

(*Received* 9 *November* 1971. *Accepted* 14 *December* 1971)

A NEW PROCEDURE has been developed to separate barium from equal molar concentrations of strontium and lead. The multivalent cations are complexed with MEDTA (1,2-diaminopropane-tetra-acetic acid) or DCTA (1,2-diaminocyclohexane-*N,N,N',N'*-tetra-acetic acid) at a pH of 10·3 or higher in ammoniacal solution. The addition of chromate does not bring about precipitation. The solution is then heated and agitated. Ammonia volatilizes from solution, causing a gradual increase in hydrogen ion concentration. Hydrogen ions compete for the chelating agent which results in a gradual increase in the free barium ion concentration. This causes a slow precipitation of barium chromate from homogeneous solution.

Both the strontium and lead chelates are more stable than the barium chelate. Therefore, the concentration of free strontium ions and free lead ions remains low throughout the precipitation of the barium chromate. Atomic-absorption measurements show that less than 0·05% of the strontium and less than 0·06% of the lead co-precipitate when MEDTA is used. About 0·15% of the strontium and about 0·03% of the lead co-precipitate when DCTA is used.

Precipitation of barium chromate has been the classical method[1] of separating barium fom strontium. The use of precipitation from homogeneous solution[2] as well as complexation[3] has improved the classical method. Complexation has also made a separation of barium from lead possible, with chromate as the precipitant.

Additional modifications based on these fundamental ideas have resulted in further improvements in the separation of barium from both strontium and lead. The method described co-precipitates only about a twelfth of the strontium co-precipitated by the earlier method,[3] and should be applicable to many other systems where cation release is required. Lower pH values can be attained by addition of acid by volatilization in a closed system.

Talanta, 1972, Vol. 19, pp. 787 to 790. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Indirect method for the determination of aluminium by atomic-absorption spectrometry using an air–acetylene flame

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

It has been reported that serious interelement interferences are observed in the atomic-absorption determination of iron under certain operating conditions using an air–acetylene flame.[1,2] When flame conditions are optimized for maximum iron absorbance to be obtained for solutions prepared in sulphate or nitrate media, cobalt, nickel and copper cause depressive interferences.[2] Maximum absorption by iron occurs in a slightly fuel-lean air–acetylene flame, but in the stoichiometric or fuel-rich flame the iron absorption falls sharply when a purely sulphate or nitrate medium is used. Under these conditions many metals cause enhancement of the iron absorbance,[3] and of these, titanium, aluminium, calcium and zirconium are notable for the very low concentrations at which they interfere. A similar interference pattern has also been observed for nickel, cobalt and chromium[3,4] and may be explained on the basis of overexcitation phenomena.[3,5]

The enhancement effect has been used to provide a sensitive indirect method for the determination of titanium in the concentration range 0·01–10 ppm.[6] This paper reports a similar method for aluminium and includes a more detailed discussion of the choice of matrix element and the interference effects in this type of procedure. Aluminium cannot normally be determined directly by using an air–acetylene flame[7] as the monoxide AlO is not sufficiently dissociated in this flame,[8] but a working range of 50–500 ppm aluminium has recently been attained in a direct procedure in the presence of ammonium fluoride.[9] Normally either a nitrous oxide–acetylene flame or an oxy-acetylene flame must be used and a detection limit of about 1 ppm may be readily obtained.[7,10,11] Unfortunately, this is not sufficiently sensitive for many routine industrial applications and the method proposed here, which has a limit approximately two orders of magnitude lower than this, may be suitable in some cases.

EXPERIMENTAL

A Perkin–Elmer 290 Atomic Absorption Spectrometer and hollow-cathode lamps were used and operated at the manufacturer's recommended settings. The standard 50-mm slot tubular burner head and the 50-mm slot high-temperature head were used for air–acetylene and nitrous oxide–acetylene flames respectively. Gas flow-rates were measured with Fischer and Porter ¼-in. bore flowmeters and corrected to atmospheric pressure. The air flow-rate was maintained at 46 l./min (equivalent to a flowmeter reading of 14·0 at a feed pressure of 35 psig) and the acetylene flow-rate varied between 2·0 and 4·8 l./min (equivalent to a flowmeter reading of 13·7 at a feed pressure of 8 psig). The optimum height of the optical beam above the burner for maximum enhancement was found to be 15 mm, and absorbance readings were recorded on a Honeywell Electronik 19 chart recorder.

Stock solutions of all the metals in sulphate medium were prepared as described previously.[6] A 1000-ppm aluminium solution was prepared from 1 g of aluminium powder dissolved in sulphuric acid and diluted to 1 litre so that the final concentration of sulphuric acid was $10^{-3}M$. Distilled water from an all-quartz still[12] was used throughout. The purity of water from other types of still was not adequate, presumably because of the effect of very small amounts of calcium on the phenomena to be described. Care must be taken to avoid the addition of chloride ions.

RESULTS AND DISCUSSION

The sharp drop in absorbance by iron (as sulphate or nitrate) which occurs in a fuel-rich air–acetylene flame has been described previously.[3,5] The enhancement effect of small amounts of aluminium on this depression of the iron signal in the fuel-rich flame is shown in Fig. 1. The enhancement for a 25-ppm iron solution gives a linear relationship between 0·25 and 1·2 ppm of aluminium. The signal became more or less constant from 2 up to at least 500 ppm aluminium. The shape and characteristics of this calibration curve and the enhancement effect itself are dependent on the geometry of the burner and optical systems and their orientation relative to one another. This would be

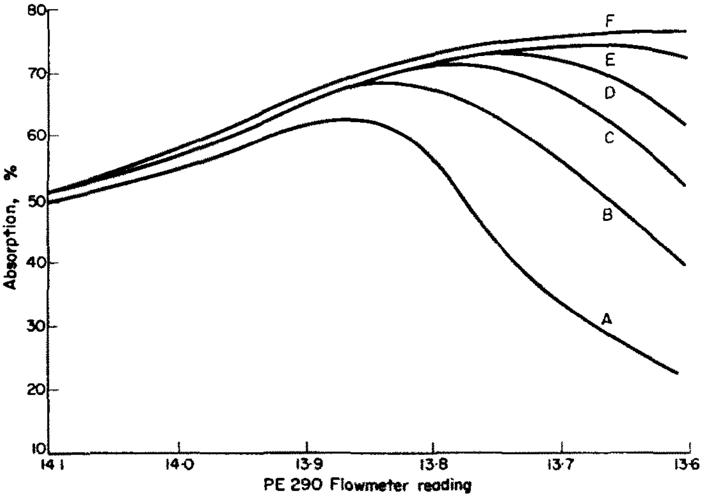


FIG. 1.—Absorption of 25 ppm iron(III) in sulphate medium as a function of acetylene flow-rate. Concentration of aluminium added: (*A*) none; (*B*) 0·5 ppm; (*C*) 1 ppm; (*D*) 2 ppm; (*E*) 10 ppm; (*F*) 500 ppm.

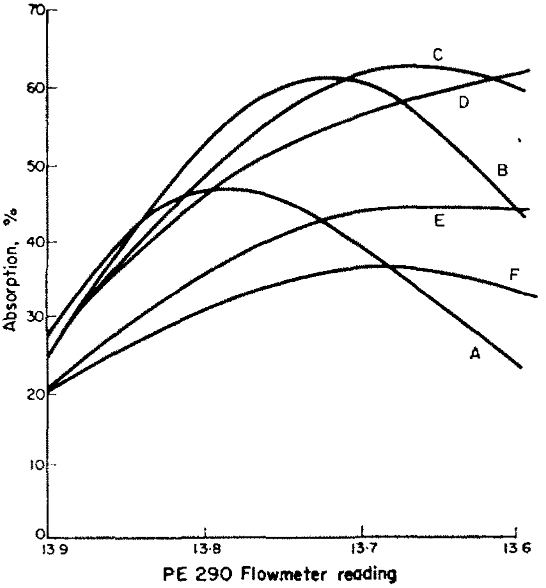


FIG. 2.—Absorption of 10 ppm chromium in sulphate medium as a function of acetylene flow-rate. Concentration of aluminium added: (*A*) none; (*B*) 0·5 ppm; (*C*) 2 ppm; (*D*) 20 ppm; (*E*) 100 ppm; (*F*) 500 ppm.

expected to depend on the particular instrument used but with the PE 290 fitted with a standard air-acetylene burner the optimum conditions for maximum sensitivity are those given above. The working range for the determination of aluminium may be varied by using different concentrations of iron. Thus, for example, the most sensitive conditions with our apparatus required use of 10 ppm of iron when the working range was 0·01–0·09 ppm of aluminium. At higher concentrations of iron, higher levels of aluminium may be detected but concentrations above 25 ppm would mean working in the range in which the direct atomic-absorption determination of aluminium is possible and the method would therefore not be particularly advantageous.

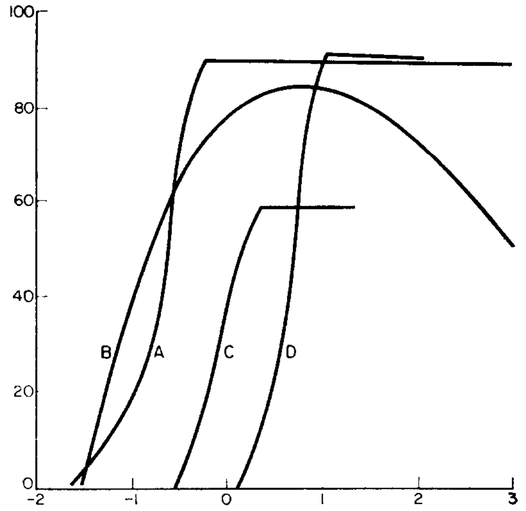


FIG. 3.—Effect of aluminium at a fuel-flow of 13·7 (meter reading) and burner height of 15 mm, on (*A*) 10 ppm of iron; (*B*) 10 ppm of chromium; (*C*) 25 ppm of cobalt; (*D*) 25 ppm of nickel; all in sulphate medium.

Aluminium gives a similar enhancement of the signals of cobalt, nickel and chromium and any of these may be used as the matrix element. The effect for chromium is shown in Fig. 2 and occurs only in the fuel-rich air–acetylene flame. At high aluminium concentrations the chromium signal does not reach a constant level but begins to fall again (Fig. 2), the maximum in the calibration curve depending on the chromium concentration, being at 5 ppm of aluminium for 10 ppm of chromium. The effect of aluminium on the atomic-absorption signals of cobalt and nickel was very similar to that for iron, although the detection of aluminium was far less sensitive with nickel. The effects of increasing aluminium concentration are shown in Fig. 3 for all four elements, which suggests that iron is the most suitable matrix element.

The operating conditions will vary from one instrument to another but they may be summarized as follows. (*i*) Slightly fuel-rich air-acetylene flame such that yellow carbon incandescence is just visible. (*ii*) Light-beam centred at 15–20 mm above the burner head. (*iii*) Matrix element iron(III) sulphate in $10^{-3}M$ sulphuric acid at an iron concentration appropriate to the working range required. (*iv*) Aluminium standards and samples prepared as sulphate and/or nitrate solutions.

We have investigated some interference effects on this procedure and these are largely as expected from the known effects of the elements on the atomic-absorption signal of iron.[3] Elements that behave in a similar manner to aluminium, *e.g.*, calcium and titanium, interfere at an equivalent concentration to the aluminium, whereas others that give an enhancement or depression of the iron signal at concentrations equivalent to the iron concentration, *e.g.*, nickel and chromium, interfere at a similar level. Thus, this method is only suitable for relatively pure aluminium solutions or for analyses in which a separation process is also included. It does, however, offer a substantial improvement in detection limit over that normally obtainable by direct atomic-absorption spectrometry, using either a nitrous oxide–acetylene or oxy-acetylene flame.

Department of Pure and Applied Chemistry
University of Strathclyde
Cathedral Street
Glasgow, C.1. Scotland

J. M. OTTAWAY
D. T. COKER*
B. SINGLETON

Summary—The enhancement of the atomic-absorption signals of iron, cobalt, nickel and chromium in a fuel-rich air–acetylene flame by small amounts of aluminium makes possible the indirect determination of aluminium in the concentration range 0·01–10 ppm. The optimization of working conditions and the occurrence of interferences are reported.

---

* Present address: Esso Research Centre, Abingdon, Berkshire.

Zusammenfassung—Die Verstärkung der Atomabsorptions-Signale von Eisen, Kobalt, Nickel und Chrom in einer fetten Luft-Acetylen-Flamme durch kleine Mengen Aluminium ermöglicht die indirekte Bestimmung von Aluminium im Konzentrationsbereich 0,01–10 ppm. Es wird über die Optimierung der Arbeitsbedingungen und das Auftreten von Störungen berichtet.

Résumé—Le renforcement des signaux d'absorption atomique des fer, cobalt, nickel et chrome dans une flamme air–acétylène riche en combustible par de petites quantités d'aluminium rend possible le dosage indirect de l'aluminium dans le domaine de concentration 0,01–10 ppm. On décrit l'optimalisation des conditions de travail et la présence d'interférences.

REFERENCES

1. K. E. Curtis, *Analyst*, 1969, **94**, 1068.
2. J. M. Ottaway, D. T. Coker, W. B. Rowston and D. R. Bhattarai, *ibid.*, 1970, **95**, 567.
3. D. T. Coker, *M.Sc. Thesis*, University of Strathclyde, 1970.
4. J. A. Davies, *M.Sc. Thesis*, University of Strathclyde, 1970.
5. D. T. Coker and J. M. Ottaway, *Nature*, 1970, **227**, 831.
6. J. M. Ottaway, D. T. Coker and J. A. Davies, *Anal. Lett.*, 1970, **3**, 385.
7. R. J. Jaworowski, R. P. Weberling and D. J. Bracco, *Anal. Chim. Acta*, 1967, **37**, 284.
8. D. T. Coker and J. M. Ottaway, *Nature*, 1971, **230**, 156.
9. A. Hofer, *Z. Anal. Chem.*, 1971, **253**, 206.
10. M. D. Amos and P. E. Thomas, *Anal. Chim. Acta*, 1965, **32**, 139.
11. T. V. Ramakrishna, P. W. West and J. W. Robinson, *ibid.*, 1967, **39**, 81.
12. E. Bishop and J. R. B. Sutton, *ibid.*, 1960, **22**, 590.

Talanta, 1972, Vol. 19, pp. 790 to 793. Pergamon Press. Printed in Northern Ireland

Precipitation of barium chromate in the presence of strontium and lead by complexation followed by volatilization of ammonia

(*Received* 9 *November* 1971. *Accepted* 14 *December* 1971)

A NEW PROCEDURE has been developed to separate barium from equal molar concentrations of strontium and lead. The multivalent cations are complexed with MEDTA (1,2-diaminopropane-tetra-acetic acid) or DCTA (1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetra-acetic acid) at a pH of 10·3 or higher in ammoniacal solution. The addition of chromate does not bring about precipitation. The solution is then heated and agitated. Ammonia volatilizes from solution, causing a gradual increase in hydrogen ion concentration. Hydrogen ions compete for the chelating agent which results in a gradual increase in the free barium ion concentration. This causes a slow precipitation of barium chromate from homogeneous solution.

Both the strontium and lead chelates are more stable than the barium chelate. Therefore, the concentration of free strontium ions and free lead ions remains low throughout the precipitation of the barium chromate. Atomic-absorption measurements show that less than 0·05% of the strontium and less than 0·06% of the lead co-precipitate when MEDTA is used. About 0·15% of the strontium and about 0·03% of the lead co-precipitate when DCTA is used.

Precipitation of barium chromate has been the classical method[1] of separating barium fom strontium. The use of precipitation from homogeneous solution[2] as well as complexation[3] has improved the classical method. Complexation has also made a separation of barium from lead possible, with chromate as the precipitant.

Additional modifications based on these fundamental ideas have resulted in further improvements in the separation of barium from both strontium and lead. The method described co-precipitates only about a twelfth of the strontium co-precipitated by the earlier method,[3] and should be applicable to many other systems where cation release is required. Lower pH values can be attained by addition of acid by volatilization in a closed system.

Zusammenfassung—Die Verstärkung der Atomabsorptions-Signale von Eisen, Kobalt, Nickel und Chrom in einer fetten Luft-Acetylen-Flamme durch kleine Mengen Aluminium ermöglicht die indirekte Bestimmung von Aluminium im Konzentrationsbereich 0,01–10 ppm. Es wird über die Optimierung der Arbeitsbedingungen und das Auftreten von Störungen berichtet.

Résumé—Le renforcement des signaux d'absorption atomique des fer, cobalt, nickel et chrome dans une flamme air–acétylène riche en combustible par de petites quantités d'aluminium rend possible le dosage indirect de l'aluminium dans le domaine de concentration 0,01–10 ppm. On décrit l'optimalisation des conditions de travail et la présence d'interférences.

REFERENCES

1. K. E. Curtis, *Analyst*, 1969, **94**, 1068.
2. J. M. Ottaway, D. T. Coker, W. B. Rowston and D. R. Bhattarai, *ibid.*, 1970, **95**, 567.
3. D. T. Coker, *M.Sc. Thesis*, University of Strathclyde, 1970.
4. J. A. Davies, *M.Sc. Thesis*, University of Strathclyde, 1970.
5. D. T. Coker and J. M. Ottaway, *Nature*, 1970, **227**, 831.
6. J. M. Ottaway, D. T. Coker and J. A. Davies, *Anal. Lett.*, 1970, **3**, 385.
7. R. J. Jaworowski, R. P. Weberling and D. J. Bracco, *Anal. Chim. Acta*, 1967, **37**, 284.
8. D. T. Coker and J. M. Ottaway, *Nature*, 1971, **230**, 156.
9. A. Hofer, *Z. Anal. Chem.*, 1971, **253**, 206.
10. M. D. Amos and P. E. Thomas, *Anal. Chim. Acta*, 1965, **32**, 139.
11. T. V. Ramakrishna, P. W. West and J. W. Robinson, *ibid.*, 1967, **39**, 81.
12. E. Bishop and J. R. B. Sutton, *ibid.*, 1960, **22**, 590.

Talanta, 1972, Vol. 19, pp. 790 to 793. Pergamon Press. Printed in Northern Ireland

Precipitation of barium chromate in the presence of strontium and lead by complexation followed by volatilization of ammonia

(*Received* 9 *November* 1971. *Accepted* 14 *December* 1971)

A NEW PROCEDURE has been developed to separate barium from equal molar concentrations of strontium and lead. The multivalent cations are complexed with MEDTA (1,2-diaminopropane-tetra-acetic acid) or DCTA (1,2-diaminocyclohexane-*N,N,N′,N′*-tetra-acetic acid) at a pH of 10·3 or higher in ammoniacal solution. The addition of chromate does not bring about precipitation. The solution is then heated and agitated. Ammonia volatilizes from solution, causing a gradual increase in hydrogen ion concentration. Hydrogen ions compete for the chelating agent which results in a gradual increase in the free barium ion concentration. This causes a slow precipitation of barium chromate from homogeneous solution.

Both the strontium and lead chelates are more stable than the barium chelate. Therefore, the concentration of free strontium ions and free lead ions remains low throughout the precipitation of the barium chromate. Atomic-absorption measurements show that less than 0·05% of the strontium and less than 0·06% of the lead co-precipitate when MEDTA is used. About 0·15% of the strontium and about 0·03% of the lead co-precipitate when DCTA is used.

Precipitation of barium chromate has been the classical method[1] of separating barium fom strontium. The use of precipitation from homogeneous solution[2] as well as complexation[3] has improved the classical method. Complexation has also made a separation of barium from lead possible, with chromate as the precipitant.

Additional modifications based on these fundamental ideas have resulted in further improvements in the separation of barium from both strontium and lead. The method described co-precipitates only about a twelfth of the strontium co-precipitated by the earlier method,[3] and should be applicable to many other systems where cation release is required. Lower pH values can be attained by addition of acid by volatilization in a closed system.

EXPERIMENTAL

Procedure

Add a sample containing about 0·5 mmole of barium (about 70 mg) to a 400-ml beaker.* Add about 50 ml of demineralized water and an excess of chelating agent.† Bring the pH of the solution to 10·3 or slightly higher by the addition of 3*M* ammonia. Add 50 ml of 0·02*M* potassium dichromate adjusted to pH 10·3 or higher.§ Dilute to about 125 ml.

Place the beaker on an oscillating hot-plate. Maintain the temperature within the range 45–60°. Keep the volume of solution reasonably constant by occasional additions of demineralized water. Within about 6–8 hr the pH of the solution will fall to 6–7, usually to 6·7–6·8. Remove the beaker from the hot-plate, stir and let stand overnight.

Filter off on a medium porosity crucible, wash with 0·001*M* potassium dichromate adjusted to pH 7·0, finally rinse with a small portion of demineralized water, and dry the precipitate at 110–120° for 2 hr.

RESULTS AND DISCUSSION

Table I gives the results obtained for the pH range of 6·7–6·8 for the final solution. In this range the ammonia is essentially removed from solution. The precipitation is also maximal in this pH range. The results show that more than 99·3% of the barium is precipitated.

TABLE I.—PRECIPITATION OF BARIUM CHROMATE

Ba found, *mg* (gravimetric)	Ba in filtrate, *mg* (atomic absorption)
71·2	0·45
71·8	0·54
71·3	0·20
71·4	0·35
71·0	0·30

Barium taken 71·7 mg (0·5 mmole); 1·0 mmole of potassium dichromate and 0·6 mmole of MEDTA added to each solution. Final pH 6·7–6·8.

Additional investigation showed that precipitation was not nearly quantitative above pH 7·0 or below pH 5·5, but within this range precipitation was at least 99% complete, being maximal over the pH range 6·0–6·8 (average 99·5–99·6%). Atomic-absorption measurements showed that up to 0·7% of the barium appeared in the filtrate (average about 0·4%).

To study the effect of pH at values lower than 6·7, a method of homogeneously increasing the hydrogen ion concentration was needed. To do this with a minimum of disturbance to the solution, either acetic or hydrochloric acid was allowed to volatilize into the solution. A polyethylene bag was placed on an oscillating plate. The beaker containing both barium and chromate was placed inside this bag. A second beaker containing either acetic or hydrochloric acid was also placed inside the bag. The bag was then closed, and the oscillating cycle started. Acid volatilized into the barium solution, causing a slow increase in hydrogen ion concentration. Even though the acid could only enter at the surface of the solution, the agitation tended to distribute it throughout the solution.

Table II gives the results obtained when strontium and lead are also present in the solution. These results show that less than 0.05% of the strontium is co-precipitated when MEDTA is used as the chelating agent. With DCTA as chelating agent, the strontium co-precipitated is about 0.16%. Less than 0·06% of the lead is co-precipitated when MEDTA is used. When DCTA is used the amount of lead co-precipitated is about 0·03% or less.

---

* For easy removal of the precipitate, spray a thin film of silicone on a new, unscratched beaker. Dry the beaker at 125° for about 1 hr.

† Enough chelating agent must be added to complex all the barium and all the cations in solution that form a more stable complex with the chelating agent than barium. An excess of about 20% is sufficient. MEDTA and DCTA give similar results. MEDTA is superior for strontium separation, DCTA for lead separation.

§ If the pH of either solution is below 10·3, a precipitation from heterogeneous solution will occur on mixing. This destroys most of the advantages of the proposed method.

TABLE II.—SEPARATION OF BARIUM CHROMATE FROM STRONTIUM AND LEAD

Ba found, *mg* (gravimetric)	Chelating agent	Other ion present	Ba in filtrate, *mg* (atomic absorption)	Sr or Pb in precipitate, *mg* (atomic absorption)
71·4	MEDTA	Sr	0·28	0·01
71·4	MEDTA	Sr	0·28	0·01
71·2	MEDTA	Sr	0·19	0·01
71·5*	MEDTA	Sr	0·40	0·02
72·1	MEDTA	Sr	0·26	0·02
71·7	MEDTA	Pb	0·03	0·06
71·4	MEDTA	Pb	0·25	0·05
72·3	DCTA	Sr	0·04	0·07
71·4	DCTA	Pb	0·23	0·03
72·2	DCTA	Pb	0·22	0·00

Barium taken 71·7 mg (0·5 mmole); 0·5 mmole of strontium or lead and 1·2 mmole of MEDTA or DCTA added to each solution. Final pH 6·7–6·8.

* pH 7·2.

The barium ion is released slowly and uniformly. Even though ammonia escapes only at the surface of the solution, the agitation used results in an essentially homogeneous solution of barium and chromate ions.

The experimental results support the conclusions drawn from a calculation involving the formation constants and solubility products. MEDTA provides the better separation from strontium, DCTA is better for lead separation.

This method has several distinct advantages over the earlier method.[8] Only about a twelfth as much strontium is co-precipitated. Furthermore, dropwise addition of a magnesium chloride solution from a burette is not required, so there is no magnesium contamination of the filtrate.

Acknowledgement—The authors wish to thank Joseph B. Johnson for the preliminary work that indicated this separation would be successful.

Science and Technology Division
Southern Illinois University
Edwardsville, Illinois 62025, U.S.A.

F. H. FIRSCHING
PAUL H. WERNER

Summary—Cation-release is used to precipitate barium chromate from homogeneous solution in the presence of lead and strontium. MEDTA or DCTA is added to complex the metal ions at pH $\geqslant$ 10·3 (adjusted with ammonia). On heating, the ammonia slowly volatilizes and the consequent increases in acidity releases the metal ion bound in the least stable chelate (barium). Precipitation is about 99·3–99·7% complete at pH 6·7–6·8, with less than 0·1% co-precipitation of lead or strontium. Lower pH values can be attained by volatilizing acetic or hydrochloric acid into the solution in a closed system.

Zusammenfassung—Zur Fällung von Bariumchromat aus homogener Lösung in Gegenwart von Blei und Strontium wurde die Kationen-Freisetzung verwendet. Zur komplexen Bindung der Metallionen wird bei pH $\geqslant$ 10,3 (mit Ammoniak eingestellt) MEDTA oder DCTA zugegeben. Beim Erhitzen geht Ammoniak langsam flüchtig und das Anwachsen der Acidität gibt das im am wenigsten stabilen Chelat gebundene Metall (Barium) frei. Die Fällung ist bei pH 6,7–8,6, zu etwa 99,3–99,7% vollständig. Mitfällung von Blei oder Strontium findet zu weniger als 0,1% statt. Niedrigere pH-Werte kann man erreichen, wenn man in einem geschlossenen System Essigsäure oder Salzsaure in die Lösung eindestillieren läßt.

Résumé—On utilise la libération de cations pour précipiter le chromate de baryum d'une solution homogène en la présence de plomb et de strontium. On ajoute MEDTA ou DCTA pour complexer les ions métalliques à pH $>$ 10,3 (ajusté par l'ammoniaque). Par chauffage, l'ammoniaque se volatilise lentement et l'accroissement conséquent de l'acidité libère l'ion métallique lié dans le chélate le moins stable (baryum). La précipitation est complète à 99,3–99,7% à pH 6,7–6,8, avec moins de 0,1% de coprécipitation du plomb ou du strontium. On peut atteindre des valeurs de pH plus basses en volatilisant de l'acide acétique ou chlorhydrique dans la solution dans un système clos.

REFERENCES

1. A. Skrabal and L. Neustadtl, *Z. Anal. Chem.*, 1905, **44**, 742.
2. L. Gordon and F. H. Firsching, *Anal. Chem.*, 1954, **26**, 759.
3. F. H. Firsching, *Talanta*, 1959, **2**, 326.

Talanta, 1972, Vol. 19, pp. 793 to 796. Pergamon Press. Printed in Northern Ireland

Catalysis of the arsenic(III)–potassium bromate reaction—I. Titrimetric determination of arsenic(III) in the presence of osmium tetroxide

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

Many studies of the titrimetric determination of arsenic(III) and antimony(III) with potassium bromate have been reported and these have been reviewed on several occasions.[1,2] In the course of a careful investigation[2] of the limiting conditions under which the titration of arsenic(III) with potassium bromate is stoichiometric, it was shown that positive errors are obtained at hydrochloric acid concentrations below 0·55*M* in the absence of added bromide and below 0·3*M* in the presence of 0·1*M* bromide (see Fig. 1). The reaction becomes extremely slow in the absence of both chloride and bromide, and gross positive errors result in, for example, sulphuric acid solution. Chloride and bromide may be considered to act as catalysts in the system through the intermediate formation of halogens, *e.g.*, for bromide,

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (1)$$

$$As(III) + Br_2 \rightarrow As(V) + 2Br^- \quad (2)$$

Chloride is less effective than bromide as a catalyst since its reaction with bromate is slower and this explains the limiting hydrochloric acid concentration being slightly higher in a bromide-free medium than in one that is 0·1*M* in bromide.

The possibility of using other species to catalyse the antimony(III) or arsenic(III) reactions with bromate seemed worth investigating with a view to extending the range of acid concentrations over which the titration is analytically feasible. This was successful only in the case of arsenic(III), the reaction of which with bromate was found to be catalysed by osmic acid. Although osmic acid has been used to catalyse a number of reactions it does not seem to have been applied previously for this one. This paper therefore reports the application of this catalyst to the titrimetric determination of arsenic(III); subsequent papers will describe methods for the catalytic determination of chloride, bromide and osmium by the arsenic(III)–bromate reaction.

EXPERIMENTAL

Reagents

A stock solution of osmium tetroxide was prepared by breaking a phial containing 1 g of osmium tetroxide under 40 ml of 0·5*M* sulphuric acid and diluting to approximately 400 ml. It was standardized iodometrically.[3]

Other solutions and reagents were prepared and standardized as described previously.[2,4] Analytical-grade reagents were used wherever possible and glass-distilled water was used throughout.

Zusammenfassung—Die Verstärkung der Atomabsorptions-Signale von Eisen, Kobalt, Nickel und Chrom in einer fetten Luft-Acetylen-Flamme durch kleine Mengen Aluminium ermöglicht die indirekte Bestimmung von Aluminium im Konzentrationsbereich 0,01–10 ppm. Es wird über die Optimierung der Arbeitsbedingungen und das Auftreten von Störungen berichtet.

Résumé—Le renforcement des signaux d'absorption atomique des fer, cobalt, nickel et chrome dans une flamme air–acétylène riche en combustible par de petites quantités d'aluminium rend possible le dosage indirect de l'aluminium dans le domaine de concentration 0,01–10 ppm. On décrit l'optimalisation des conditions de travail et la présence d'interférences.

REFERENCES

1. K. E. Curtis, *Analyst*, 1969, **94**, 1068.
2. J. M. Ottaway, D. T. Coker, W. B. Rowston and D. R. Bhattarai, *ibid.*, 1970, **95**, 567.
3. D. T. Coker, *M.Sc. Thesis*, University of Strathclyde, 1970.
4. J. A. Davies, *M.Sc. Thesis*, University of Strathclyde, 1970.
5. D. T. Coker and J. M. Ottaway, *Nature*, 1970, **227**, 831.
6. J. M. Ottaway, D. T. Coker and J. A. Davies, *Anal. Lett.*, 1970, **3**, 385.
7. R. J. Jaworowski, R. P. Weberling and D. J. Bracco, *Anal. Chim. Acta*, 1967, **37**, 284.
8. D. T. Coker and J. M. Ottaway, *Nature*, 1971, **230**, 156.
9. A. Hofer, *Z. Anal. Chem.*, 1971, **253**, 206.
10. M. D. Amos and P. E. Thomas, *Anal. Chim. Acta*, 1965, **32**, 139.
11. T. V. Ramakrishna, P. W. West and J. W. Robinson, *ibid.*, 1967, **39**, 81.
12. E. Bishop and J. R. B. Sutton, *ibid.*, 1960, **22**, 590.

Talanta, 1972, Vol. 19, pp. 790 to 793. Pergamon Press. Printed in Northern Ireland

Precipitation of barium chromate in the presence of strontium and lead by complexation followed by volatilization of ammonia

(*Received* 9 *November* 1971. *Accepted* 14 *December* 1971)

A NEW PROCEDURE has been developed to separate barium from equal molar concentrations of strontium and lead. The multivalent cations are complexed with MEDTA (1,2-diaminopropane-tetra-acetic acid) or DCTA (1,2-diaminocyclohexane-*N,N,N',N'*-tetra-acetic acid) at a pH of 10·3 or higher in ammoniacal solution. The addition of chromate does not bring about precipitation. The solution is then heated and agitated. Ammonia volatilizes from solution, causing a gradual increase in hydrogen ion concentration. Hydrogen ions compete for the chelating agent which results in a gradual increase in the free barium ion concentration. This causes a slow precipitation of barium chromate from homogeneous solution.

Both the strontium and lead chelates are more stable than the barium chelate. Therefore, the concentration of free strontium ions and free lead ions remains low throughout the precipitation of the barium chromate. Atomic-absorption measurements show that less than 0·05% of the strontium and less than 0·06% of the lead co-precipitate when MEDTA is used. About 0·15% of the strontium and about 0·03% of the lead co-precipitate when DCTA is used.

Precipitation of barium chromate has been the classical method[1] of separating barium fom strontium. The use of precipitation from homogeneous solution[2] as well as complexation[3] has improved the classical method. Complexation has also made a separation of barium from lead possible, with chromate as the precipitant.

Additional modifications based on these fundamental ideas have resulted in further improvements in the separation of barium from both strontium and lead. The method described co-precipitates only about a twelfth of the strontium co-precipitated by the earlier method,[3] and should be applicable to many other systems where cation release is required. Lower pH values can be attained by addition of acid by volatilization in a closed system.

EXPERIMENTAL

Procedure

Add a sample containing about 0·5 mmole of barium (about 70 mg) to a 400-ml beaker.* Add about 50 ml of demineralized water and an excess of chelating agent.† Bring the pH of the solution to 10·3 or slightly higher by the addition of 3*M* ammonia. Add 50 ml of 0·02*M* potassium dichromate adjusted to pH 10·3 or higher.§ Dilute to about 125 ml.

Place the beaker on an oscillating hot-plate. Maintain the temperature within the range 45–60°. Keep the volume of solution reasonably constant by occasional additions of demineralized water. Within about 6–8 hr the pH of the solution will fall to 6–7, usually to 6·7–6·8. Remove the beaker from the hot-plate, stir and let stand overnight.

Filter off on a medium porosity crucible, wash with 0·001*M* potassium dichromate adjusted to pH 7·0, finally rinse with a small portion of demineralized water, and dry the precipitate at 110–120° for 2 hr.

RESULTS AND DISCUSSION

Table I gives the results obtained for the pH range of 6·7–6·8 for the final solution. In this range the ammonia is essentially removed from solution. The precipitation is also maximal in this pH range. The results show that more than 99·3% of the barium is precipitated.

TABLE I.—PRECIPITATION OF BARIUM CHROMATE

Ba found, *mg* (gravimetric)	Ba in filtrate, *mg* (atomic absorption)
71·2	0·45
71·8	0·54
71·3	0·20
71·4	0·35
71·0	0·30

Barium taken 71·7 mg (0·5 mmole); 1·0 mmole of potassium dichromate and 0·6 mmole of MEDTA added to each solution. Final pH 6·7–6·8.

Additional investigation showed that precipitation was not nearly quantitative above pH 7·0 or below pH 5·5, but within this range precipitation was at least 99% complete, being maximal over the pH range 6·0–6·8 (average 99·5–99·6%). Atomic-absorption measurements showed that up to 0·7% of the barium appeared in the filtrate (average about 0·4%).

To study the effect of pH at values lower than 6·7, a method of homogeneously increasing the hydrogen ion concentration was needed. To do this with a minimum of disturbance to the solution, either acetic or hydrochloric acid was allowed to volatilize into the solution. A polyethylene bag was placed on an oscillating plate. The beaker containing both barium and chromate was placed inside this bag. A second beaker containing either acetic or hydrochloric acid was also placed inside the bag. The bag was then closed, and the oscillating cycle started. Acid volatilized into the barium solution, causing a slow increase in hydrogen ion concentration. Even though the acid could only enter at the surface of the solution, the agitation tended to distribute it throughout the solution.

Table II gives the results obtained when strontium and lead are also present in the solution. These results show that less than 0.05% of the strontium is co-precipitated when MEDTA is used as the chelating agent. With DCTA as chelating agent, the strontium co-precipitated is about 0.16%. Less than 0·06% of the lead is co-precipitated when MEDTA is used. When DCTA is used the amount of lead co-precipitated is about 0·03% or less.

* For easy removal of the precipitate, spray a thin film of silicone on a new, unscratched beaker. Dry the beaker at 125° for about 1 hr.

† Enough chelating agent must be added to complex all the barium and all the cations in solution that form a more stable complex with the chelating agent than barium. An excess of about 20% is sufficient. MEDTA and DCTA give similar results. MEDTA is superior for strontium separation, DCTA for lead separation.

§ If the pH of either solution is below 10·3, a precipitation from heterogeneous solution will occur on mixing. This destroys most of the advantages of the proposed method.

TABLE II.—SEPARATION OF BARIUM CHROMATE FROM STRONTIUM AND LEAD

Ba found, *mg* (gravimetric)	Chelating agent	Other ion present	Ba in filtrate, *mg* (atomic absorption)	Sr or Pb in precipitate, *mg* (atomic absorption)
71·4	MEDTA	Sr	0·28	0·01
71·4	MEDTA	Sr	0·28	0·01
71·2	MEDTA	Sr	0·19	0·01
71·5*	MEDTA	Sr	0·40	0·02
72·1	MEDTA	Sr	0·26	0·02
71·7	MEDTA	Pb	0·03	0·06
71·4	MEDTA	Pb	0·25	0·05
72·3	DCTA	Sr	0·04	0·07
71·4	DCTA	Pb	0·23	0·03
72·2	DCTA	Pb	0·22	0·00

Barium taken 71·7 mg (0·5 mmole); 0·5 mmole of strontium or lead and 1·2 mmole of MEDTA or DCTA added to each solution. Final pH 6·7–6·8.

* pH 7·2.

The barium ion is released slowly and uniformly. Even though ammonia escapes only at the surface of the solution, the agitation used results in an essentially homogeneous solution of barium and chromate ions.

The experimental results support the conclusions drawn from a calculation involving the formation constants and solubility products. MEDTA provides the better separation from strontium, DCTA is better for lead separation.

This method has several distinct advantages over the earlier method.[8] Only about a twelfth as much strontium is co-precipitated. Furthermore, dropwise addition of a magnesium chloride solution from a burette is not required, so there is no magnesium contamination of the filtrate.

Acknowledgement—The authors wish to thank Joseph B. Johnson for the preliminary work that indicated this separation would be successful.

Science and Technology Division
Southern Illinois University
Edwardsville, Illinois 62025, *U.S.A.*

F. H. FIRSCHING
PAUL H. WERNER

Summary—Cation-release is used to precipitate barium chromate from homogeneous solution in the presence of lead and strontium. MEDTA or DCTA is added to complex the metal ions at pH $\geqslant$ 10·3 (adjusted with ammonia). On heating, the ammonia slowly volatilizes and the consequent increases in acidity releases the metal ion bound in the least stable chelate (barium). Precipitation is about 99·3–99·7% complete at pH 6·7–6·8, with less than 0·1% co-precipitation of lead or strontium. Lower pH values can be attained by volatilizing acetic or hydrochloric acid into the solution in a closed system.

Zusammenfassung—Zur Fällung von Bariumchromat aus homogener Lösung in Gegenwart von Blei und Strontium wurde die Kationen-Freisetzung verwendet. Zur komplexen Bindung der Metallionen wird bei pH $\geqslant$ 10,3 (mit Ammoniak eingestellt) MEDTA oder DCTA zugegeben. Beim Erhitzen geht Ammoniak langsam flüchtig und das Anwachsen der Acidität gibt das im am wenigsten stabilen Chelat gebundene Metall (Barium) frei. Die Fällung ist bei pH 6,7–8,6, zu etwa 99,3–99,7% vollständig. Mitfällung von Blei oder Strontium findet zu weniger als 0,1% statt. Niedrigere pH-Werte kann man erreichen, wenn man in einem geschlossenen System Essigsäure oder Salzsaure in die Lösung eindestillieren läßt.

Résumé—On utilise la libération de cations pour précipiter le chromate de baryum d'une solution homogène en la présence de plomb et de strontium. On ajoute MEDTA ou DCTA pour complexer les ions métalliques à pH > 10,3 (ajusté par l'ammoniaque). Par chauffage, l'ammoniaque se volatilise lentement et l'accroissement conséquent de l'acidité libère l'ion métallique lié dans le chélate le moins stable (baryum). La précipitation est complète à 99,3–99,7% à pH 6,7–6,8, avec moins de 0,1% de coprécipitation du plomb ou du strontium. On peut atteindre des valeurs de pH plus basses en volatilisant de l'acide acétique ou chlorhydrique dans la solution dans un système clos.

REFERENCES

1. A. Skrabal and L. Neustadtl, *Z. Anal. Chem.*, 1905, **44**, 742.
2. L. Gordon and F. H. Firsching, *Anal. Chem.*, 1954, **26**, 759.
3. F. H. Firsching, *Talanta*, 1959, **2**, 326.

Talanta, 1972, Vol. 19, pp. 793 to 796. Pergamon Press. Printed in Northern Ireland

Catalysis of the arsenic(III)–potassium bromate reaction—I. Titrimetric determination of arsenic(III) in the presence of osmium tetroxide

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

MANY STUDIES of the titrimetric determination of arsenic(III) and antimony(III) with potassium bromate have been reported and these have been reviewed on several occasions.[1,2] In the course of a careful investigation[2] of the limiting conditions under which the titration of arsenic(III) with potassium bromate is stoichiometric, it was shown that positive errors are obtained at hydrochloric acid concentrations below 0·55*M* in the absence of added bromide and below 0·3*M* in the presence of 0·1*M* bromide (see Fig. 1). The reaction becomes extremely slow in the absence of both chloride and bromide, and gross positive errors result in, for example, sulphuric acid solution. Chloride and bromide may be considered to act as catalysts in the system through the intermediate formation of halogens, *e.g.*, for bromide,

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (1)$$

$$As(III) + Br_2 \rightarrow As(V) + 2Br^- \quad (2)$$

Chloride is less effective than bromide as a catalyst since its reaction with bromate is slower and this explains the limiting hydrochloric acid concentration being slightly higher in a bromide-free medium than in one that is 0·1*M* in bromide.

The possibility of using other species to catalyse the antimony(III) or arsenic(III) reactions with bromate seemed worth investigating with a view to extending the range of acid concentrations over which the titration is analytically feasible. This was successful only in the case of arsenic(III), the reaction of which with bromate was found to be catalysed by osmic acid. Although osmic acid has been used to catalyse a number of reactions it does not seem to have been applied previously for this one. This paper therefore reports the application of this catalyst to the titrimetric determination of arsenic(III); subsequent papers will describe methods for the catalytic determination of chloride, bromide and osmium by the arsenic(III)–bromate reaction.

EXPERIMENTAL

Reagents

A stock solution of osmium tetroxide was prepared by breaking a phial containing 1 g of osmium tetroxide under 40 ml of 0·5*M* sulphuric acid and diluting to approximately 400 ml. It was standardized iodometrically.[3]

Other solutions and reagents were prepared and standardized as described previously.[2,4] Analytical-grade reagents were used wherever possible and glass-distilled water was used throughout.

Résumé—On utilise la libération de cations pour précipiter le chromate de baryum d'une solution homogène en la présence de plomb et de strontium. On ajoute MEDTA ou DCTA pour complexer les ions métalliques à pH > 10,3 (ajusté par l'ammoniaque). Par chauffage, l'ammoniaque se volatilise lentement et l'accroissement conséquent de l'acidité libère l'ion métallique lié dans le chélate le moins stable (baryum). La précipitation est complète à 99,3–99,7 % à pH 6,7–6,8, avec moins de 0,1 % de coprécipitation du plomb ou du strontium. On peut atteindre des valeurs de pH plus basses en volatilisant de l'acide acétique ou chlorhydrique dans la solution dans un système clos.

REFERENCES

1. A. Skrabal and L. Neustadtl, *Z. Anal. Chem.*, 1905, **44**, 742.
2. L. Gordon and F. H. Firsching, *Anal. Chem.*, 1954, **26**, 759.
3. F. H. Firsching, *Talanta*, 1959, **2**, 326.

Talanta, 1972, Vol. 19, pp. 793 to 796. Pergamon Press. Printed in Northern Ireland

Catalysis of the arsenic(III)–potassium bromate reaction—I. Titrimetric determination of arsenic(III) in the presence of osmium tetroxide

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

Many studies of the titrimetric determination of arsenic(III) and antimony(III) with potassium bromate have been reported and these have been reviewed on several occasions.[1,2] In the course of a careful investigation[2] of the limiting conditions under which the titration of arsenic(III) with potassium bromate is stoichiometric, it was shown that positive errors are obtained at hydrochloric acid concentrations below $0{\cdot}55M$ in the absence of added bromide and below $0{\cdot}3M$ in the presence of $0{\cdot}1M$ bromide (see Fig. 1). The reaction becomes extremely slow in the absence of both chloride and bromide, and gross positive errors result in, for example, sulphuric acid solution. Chloride and bromide may be considered to act as catalysts in the system through the intermediate formation of halogens, *e.g.*, for bromide,

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (1)$$

$$As(III) + Br_2 \rightarrow As(V) + 2Br^- \qquad (2)$$

Chloride is less effective than bromide as a catalyst since its reaction with bromate is slower and this explains the limiting hydrochloric acid concentration being slightly higher in a bromide-free medium than in one that is $0{\cdot}1M$ in bromide.

The possibility of using other species to catalyse the antimony(III) or arsenic(III) reactions with bromate seemed worth investigating with a view to extending the range of acid concentrations over which the titration is analytically feasible. This was successful only in the case of arsenic(III), the reaction of which with bromate was found to be catalysed by osmic acid. Although osmic acid has been used to catalyse a number of reactions it does not seem to have been applied previously for this one. This paper therefore reports the application of this catalyst to the titrimetric determination of arsenic(III); subsequent papers will describe methods for the catalytic determination of chloride, bromide and osmium by the arsenic(III)–bromate reaction.

EXPERIMENTAL

Reagents

A stock solution of osmium tetroxide was prepared by breaking a phial containing 1 g of osmium tetroxide under 40 ml of $0{\cdot}5M$ sulphuric acid and diluting to approximately 400 ml. It was standardized iodometrically.[3]

Other solutions and reagents were prepared and standardized as described previously.[2,4] Analytical-grade reagents were used wherever possible and glass-distilled water was used throughout.

Procedures

The visual titration procedure has been described previously.[2] Potentiometric titrations were performed in a 250-ml beaker, using a bright platinum wire (1 in., 22 swg) indicator electrode with a saturated calomel reference electrode. The equivalence-point volume of titration solution was arranged to be as near 150 ml as possible and in titrations for which the end-point concentration of acid is quoted, the volume of the titration solution at the end-point was measured and the concentration calculated for this volume. For titrations conducted in the absence of air, all reagents and titrand solution were deaerated with "White-spot" nitrogen for 15 min before titration and during titration nitrogen was passed over the surface of the titrand.

RESULTS AND DISCUSSION

A number of compounds were investigated as possible catalysts, amongst them being osmium(VIII), ruthenium(III), rhenium(VII), gold(III), thallium(III), molybdenum(VI), tungsten(VI), vanadium(V) and iridium(IV). Some of these are well known to catalyse other reactions involving arsenic(III), for example, ruthenium[5] and osmium[6-8] catalyse the cerium(IV)-arsenic(III) reaction and vanadium and molybdenum are known[9,10] to catalyse a number of other bromate reactions. The only compound which was found to be effective in either of the reactions under investigation was osmium tetroxide which catalysed the arsenic(III)-bromate reaction. Reaction in the presence of osmium(VIII) is stoichiometric under a wide range of acid conditions and the error curves obtained in the presence of varying concentrations of sulphuric acid (curve *d*) and hydrochloric acid (curve *c*) are shown in Fig. 1 together with the error curves previously reported[2] for titrations in hydrochloric acid media in the absence of osmium. Results on the straight line are accurate to within 0·01 ml in a 25-ml titration and are in agreement with the dry weights of arsenious oxide and potassium bromate used to prepare the standard solutions. The amount of osmic acid stock solution added to each titration does not appear critical since the smallest drop is sufficient to allow the reaction to proceed at a satisfactory rate. Since the indicator mechanism of all known bromatometric and bromometric indicators is by reaction with bromine,[11] none is suitable for the titration in the presence of osmium(VIII), as bromine is not generated rapidly enough at the equivalence point at acid concentrations below 0·1*M*. It is possible to use such indicators at high acid concentrations, above 1*M*, when reaction of the first excess of bromate with the bromide generated by the reduction of bromate up to the equivalence point to form bromine, is fast.[2] To cover the whole range with one method of indication, potentiometry was used. At lower acid concentrations, the electrode takes a considerable time to attain a steady potential in the region of the equivalence point, but at 0·1*M* acid and above the maximum time was 30 sec, and the potential break is sufficiently large (400 mV) for even

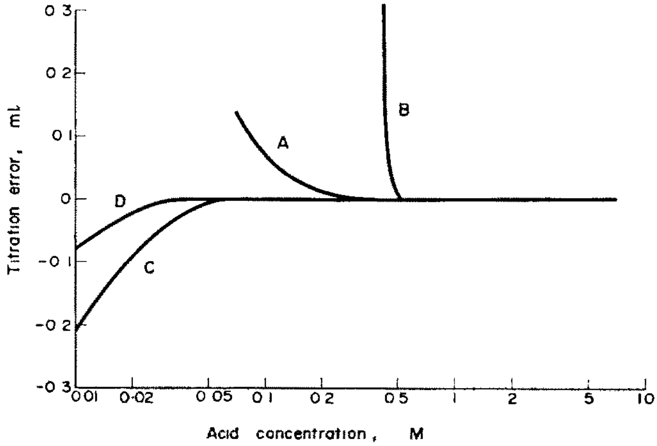


FIG. 1.—Errors in the potentiometric titration of 25 ml of 0·05*M* arsenic(III) with 0·01667*M* potassium bromate in various media.
(A) Initial bromide concentration 0·1*M*, hydrochloric acid.[2]
(B) Initially bromide-free, hydrochloric acid.[2]
(C) Two drops 0·01*M* osmic acid, hydrochloric acid.
(D) Two drops 0·01*M* osmic acid, sulphuric acid.

continuous titration to be possible under these conditions. In acid concentrations below $0{\cdot}05M$, negative titration errors were obtained, which increased in size with a decrease in hydrogen ion concentration. That this was caused by a slow reaction seemed unlikely since in that case positive errors would have been expected. The errors were not related to the presence of bromide, generated from bromate, since addition of mercuric nitrate to complex the bromide was without effect on the error. However when the titrations were performed in a closed titration vessel under an inert atmosphere, the negative errors disappeared. This suggests that oxygen is involved in a secondary oxidation process which may be an induced reaction, similar to that found for antimony(III).[4] Although the titration reaction of antimony(III) with potassium bromate was not catalysed by osmium(VIII), the negative errors obtained at concentrations of hydrochloric acid between $0{\cdot}3$ and $1{\cdot}0M$ were found to be considerably increased in the presence of osmium(VIII). Thus the extent of induced air oxidation of antimony(III) is apparently increased by osmium and a similar reaction may be the cause of the negative errors shown in Fig. 1 for the titration of arsenic(III) at low acid concentrations. This hypothesis is also supported by the fact that the negative error was found to increase with a decrease in the rate of titration.[12] However this aspect has not been pursued.

The use of osmic acid as a catalyst in the titration of arsenic(III) thus offers the advantage of a wider acid concentration range than is available in the presence of chloride or bromide and also avoids the intermediate formation of halogens with the possibility of loss of titrant by volatilization. In addition it appears to offer the possibility of determining arsenic(III) in the presence of antimony(III) by selective catalysis of the arsenic(III) reaction. We have attempted to realize this possibility, using both potentiometric and thermometric determination of the end-point. Fairly low acid concentration is required, *i.e.*, $0{\cdot}1M$, as otherwise the bromide produced from the reaction of arsenic(III) with bromate, reacts with bromate after the end-point, producing bromine which initiates the oxidation of the antimony(III). We have so far been unable to find suitable conditions for this selective determination of arsenic(III), as the arsenic(V) produced reacts at least partially with antimony(III) under those conditions suitable for the selective catalysis. For the titration of arsenic(III) alone, the recommended conditions are a solution of the arsenic(III) sample in $0{\cdot}1M$ acid (either sulphuric or hydrochloric) with one or two drops of $0{\cdot}01M$ osmic acid catalyst added. The arsenic(III) may then by titrated directly with potassium bromate potentiometrically.

Chemistry Department
University of Strathclyde
Cathedral Street, Glasgow, C.1

D. R. BHATTARAI*
J. M. OTTAWAY

Summary—The range of acid concentration available for the titration of arsenic(III) with bromate is considerably extended by the use of osmium tetroxide as catalyst in preference to the use of hydrochloric acid or hydrochloric acid–potassium bromide media. The acid concentration range over which reaction is stoichiometric has been established by potentiometric titration.

Zusammenfassung—Der Bereich an Säurekonzentrationen für die Titration von Arsen(III) mit Bromat läßt sich durch die Verwendung von Osmiumtetroxid als Katalysator beträchtlich ausdehnen, verglichen mit salzsauren oder salzsauren, Kalium-bromid enthaltenden Medien. Durch potentiometrische Titration wurde der Säurekonzentrationsbereich ermittelt, in dem die Reaktion stöchiometrisch abläuft.

Résumé—On étend considérablement le domaine de concentration d'acide convenable pour le dosage de l'arsenic(III) par le bromate en utilisant le tétroxyde d'osmium comme catalyseur de préférence à des milieux acide chlorhydrique ou acide chlorhydrique–bromure de potassium. On a établi le domaine de concentration d'acide dans lequel la réaction est stoechiométrique par titrage potentiométrique.

REFERENCES

1. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957.
2. J. M. Ottaway and E. Bishop, *Anal. Chim. Acta* **195, 33,** 153.
3. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1966.
4. E. Bishop, J. M. Ottaway and G. D. Short, *Anal. Chim. Acta*, 1962, **27**, 528.

* Present address: Nepal Geological Survey, Kathmandu, Nepal.

5. C. Surasiti and E. B. Sandell, *ibid.*, 1960, **22**, 261.
6. E. B. Sandell and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934, **56**, 1426.
7. R. L. Habig, H. L. Pardue and J. B. Worthington, *Anal. Chem.*, 1967, **39**, 600.
8. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
9. L. Szebelledy and M. Ajtai, *Mikrochem. Mikrochim. Acta*, 1938, **25**, 258; 1939, **26**, 72, 75 and 87.
10. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon, Oxford, 1966.
11. E. Bishop, in *Indicators*, Vol. 2, ed. E. Bishop, Pergamon, Oxford, 1972.
12. L. Csanji, *Acta. Chim. Acad. Sci. Hung.*, 1961, **26**, 29.

Talanta, 1972, Vol. 19, pp. 796 to 798. Pergamon Press. Printed in Northern Ireland

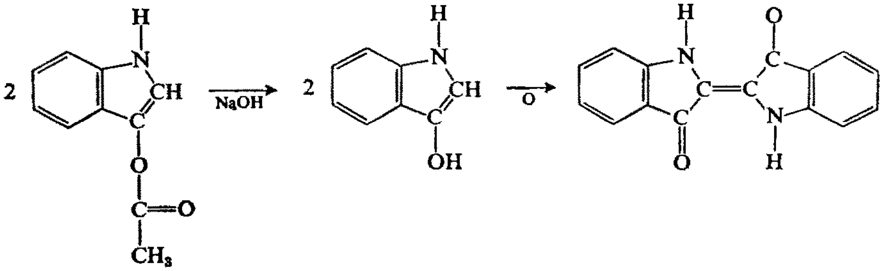
Rapid colorimetric determination of indoxyl acetate

(*Received* 31 *October* 1971. *Accepted* 3 *December* 1971)

AN ESTIMATION of cholinesterase activity can be made by following the colour or fluorescence changes produced in indoxyl acetate or other substrates.[1,2] When used to detect anticholinesterase agents, the proper colorimetric response per unit quantity of indoxyl acetate is vital, and thus a rapid method to assess the quality of each batch of recrystallized indoxyl acetate is useful. A simple colorimetric method devised for this purpose is presented here.

The determination of indoxyl (3-hydroxyindole) compounds has been widely studied as indoxyl compounds are formed by metabolic processes in the body, and certain intestinal and renal conditions are characterized by abnormally high concentrations of indoxyl and related compounds in the blood and/or urine of persons so afflicted. Several analytical methods[3-7] are routinely employed for indoxyl determination in blood or urine. These methods were generally considered too complicated for our use.

In the detection test reaction, a wetted mixture of indoxyl acetate and potassium ferricyanide reacts with acetycholinesterase to produce a blue colour when no anticholinesterase agents are present. Feigl[8] describes the similar reaction of indican, an indoxyl glucoside occurring in plants, with the enzyme emulsin. The reaction involves hydrolysis of the indican to indoxyl, which in turn is oxidized to indigo. As has been shown,[9] indoxyl compounds in urinary extracts undergo similar colour changes when treated with alkali and a mild oxidizing agent. These reactions, summarized below for indoxyl acetate, are the basis of our rapid colorimetric method.



Indoxyl acetate Indoxyl Indigo

EXPERIMENTAL

Reagents

Indoxyl acetate calibration solution. Dissolve 25 mg of recrystallized indoxyl acetate (m.p. 128° or above) in 50 ml of methanol. The solution should be freshly prepared and protected from light.

Sodium hydroxide solution, 0.1*M in methanol.*

Procedure

Prepare a solution to contain 25 mg of the indoxyl acetate to be tested, per 50 ml of methanol. Transfer 0·5 ml of this solution by Mohr pipette into a 10-ml volumetric flask, and dilute with water to approximately 9 ml. Add (Mohr pipette) 0.3 ml of methanolic 0.1*M* sodium hydroxide, mix, let

Résumé—On utilise la libération de cations pour précipiter le chromate de baryum d'une solution homogène en la présence de plomb et de strontium. On ajoute MEDTA ou DCTA pour complexer les ions métalliques à pH > 10,3 (ajusté par l'ammoniaque). Par chauffage, l'ammoniaque se volatilise lentement et l'accroissement conséquent de l'acidité libère l'ion métallique lié dans le chélate le moins stable (baryum). La précipitation est complète à 99,3–99,7% à pH 6,7–6,8, avec moins de 0,1% de coprécipitation du plomb ou du strontium. On peut atteindre des valeurs de pH plus basses en volatilisant de l'acide acétique ou chlorhydrique dans la solution dans un système clos.

REFERENCES

1. A. Skrabal and L. Neustadtl, *Z. Anal. Chem.*, 1905, **44**, 742.
2. L. Gordon and F. H. Firsching, *Anal. Chem.*, 1954, **26**, 759.
3. F. H. Firsching, *Talanta*, 1959, **2**, 326.

Talanta, 1972, Vol. 19, pp. 793 to 796. Pergamon Press. Printed in Northern Ireland

Catalysis of the arsenic(III)–potassium bromate reaction—I. Titrimetric determination of arsenic(III) in the presence of osmium tetroxide

(*Received* 9 *November* 1971. *Accepted* 13 *December* 1971)

Many studies of the titrimetric determination of arsenic(III) and antimony(III) with potassium bromate have been reported and these have been reviewed on several occasions.[1,2] In the course of a careful investigation[2] of the limiting conditions under which the titration of arsenic(III) with potassium bromate is stoichiometric, it was shown that positive errors are obtained at hydrochloric acid concentrations below 0·55*M* in the absence of added bromide and below 0·3*M* in the presence of 0·1*M* bromide (see Fig. 1). The reaction becomes extremely slow in the absence of both chloride and bromide, and gross positive errors result in, for example, sulphuric acid solution. Chloride and bromide may be considered to act as catalysts in the system through the intermediate formation of halogens, *e.g.*, for bromide,

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (1)$$

$$As(III) + Br_2 \rightarrow As(V) + 2Br^- \qquad (2)$$

Chloride is less effective than bromide as a catalyst since its reaction with bromate is slower and this explains the limiting hydrochloric acid concentration being slightly higher in a bromide-free medium than in one that is 0·1*M* in bromide.

The possibility of using other species to catalyse the antimony(III) or arsenic(III) reactions with bromate seemed worth investigating with a view to extending the range of acid concentrations over which the titration is analytically feasible. This was successful only in the case of arsenic(III), the reaction of which with bromate was found to be catalysed by osmic acid. Although osmic acid has been used to catalyse a number of reactions it does not seem to have been applied previously for this one. This paper therefore reports the application of this catalyst to the titrimetric determination of arsenic(III); subsequent papers will describe methods for the catalytic determination of chloride, bromide and osmium by the arsenic(III)–bromate reaction.

EXPERIMENTAL

Reagents

A stock solution of osmium tetroxide was prepared by breaking a phial containing 1 g of osmium tetroxide under 40 ml of 0·5*M* sulphuric acid and diluting to approximately 400 ml. It was standardized iodometrically.[3]

Other solutions and reagents were prepared and standardized as described previously.[2,4] Analytical-grade reagents were used wherever possible and glass-distilled water was used throughout.

Procedures

The visual titration procedure has been described previously.[2] Potentiometric titrations were performed in a 250-ml beaker, using a bright platinum wire (1 in., 22 swg) indicator electrode with a saturated calomel reference electrode. The equivalence-point volume of titration solution was arranged to be as near 150 ml as possible and in titrations for which the end-point concentration of acid is quoted, the volume of the titration solution at the end-point was measured and the concentration calculated for this volume. For titrations conducted in the absence of air, all reagents and titrand solution were deaerated with "White-spot" nitrogen for 15 min before titration and during titration nitrogen was passed over the surface of the titrand.

RESULTS AND DISCUSSION

A number of compounds were investigated as possible catalysts, amongst them being osmium(VIII), ruthenium(III), rhenium(VII), gold(III), thallium(III), molybdenum(VI), tungsten(VI), vanadium(V) and iridium(IV). Some of these are well known to catalyse other reactions involving arsenic(III), for example, ruthenium[5] and osmium[6–8] catalyse the cerium(IV)–arsenic(III) reaction and vanadium and molybdenum are known[9,10] to catalyse a number of other bromate reactions. The only compound which was found to be effective in either of the reactions under investigation was osmium tetroxide which catalysed the arsenic(III)–bromate reaction. Reaction in the presence of osmium(VIII) is stoichiometric under a wide range of acid conditions and the error curves obtained in the presence of varying concentrations of sulphuric acid (curve *d*) and hydrochloric acid (curve *c*) are shown in Fig. 1 together with the error curves previously reported[8] for titrations in hydrochloric acid media in the absence of osmium. Results on the straight line are accurate to within 0·01 ml in a 25-ml titration and are in agreement with the dry weights of arsenious oxide and potassium bromate used to prepare the standard solutions. The amount of osmic acid stock solution added to each titration does not appear critical since the smallest drop is sufficient to allow the reaction to proceed at a satisfactory rate. Since the indicator mechanism of all known bromatometric and bromometric indicators is by reaction with bromine,[11] none is suitable for the titration in the presence of osmium(VIII), as bromine is not generated rapidly enough at the equivalence point at acid concentrations below 0·1*M*. It is possible to use such indicators at high acid concentrations, above 1*M*, when reaction of the first excess of bromate with the bromide generated by the reduction of bromate up to the equivalence point to form bromine, is fast.[2] To cover the whole range with one method of indication, potentiometry was used. At lower acid concentrations, the electrode takes a considerable time to attain a steady potential in the region of the equivalence point, but at 0·1*M* acid and above the maximum time was 30 sec, and the potential break is sufficiently large (400 mV) for even

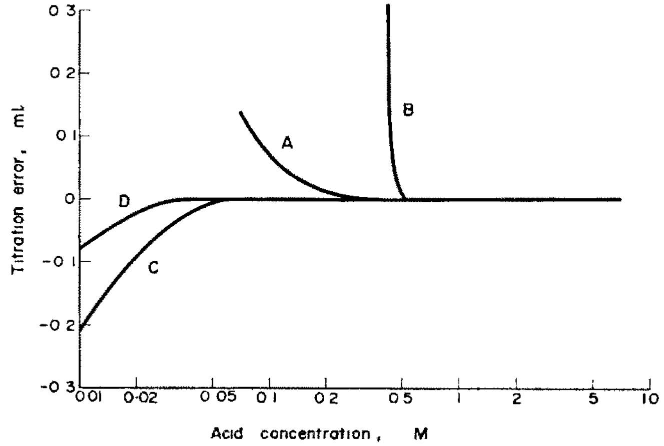


FIG. 1.—Errors in the potentiometric titration of 25 ml of 0·05*M* arsenic(III) with 0·01667*M* potassium bromate in various media.

(A) Initial bromide concentration 0·1*M*, hydrochloric acid.[8]
(B) Initially bromide-free, hydrochloric acid.[2]
(C) Two drops 0·01*M* osmic acid, hydrochloric acid.
(D) Two drops 0·01*M* osmic acid, sulphuric acid.

continuous titration to be possible under these conditions. In acid concentrations below 0·05M, negative titration errors were obtained, which increased in size with a decrease in hydrogen ion concentration. That this was caused by a slow reaction seemed unlikely since in that case positive errors would have been expected. The errors were not related to the presence of bromide, generated from bromate, since addition of mercuric nitrate to complex the bromide was without effect on the error. However when the titrations were performed in a closed titration vessel under an inert atmosphere, the negative errors disappeared. This suggests that oxygen is involved in a secondary oxidation process which may be an induced reaction, similar to that found for antimony(III).[4] Although the titration reaction of antimony(III) with potassium bromate was not catalysed by osmium(VIII), the negative errors obtained at concentrations of hydrochloric acid between 0·3 and 1·0M were found to be considerably increased in the presence of osmium(VIII). Thus the extent of induced air oxidation of antimony(III) is apparently increased by osmium and a similar reaction may be the cause of the negative errors shown in Fig. 1 for the titration of arsenic(III) at low acid concentrations. This hypothesis is also supported by the fact that the negative error was found to increase with a decrease in the rate of titration.[12] However this aspect has not been pursued.

The use of osmic acid as a catalyst in the titration of arsenic(III) thus offers the advantage of a wider acid concentration range than is available in the presence of chloride or bromide and also avoids the intermediate formation of halogens with the possibility of loss of titrant by volatilization. In addition it appears to offer the possibility of determining arsenic(III) in the presence of antimony(III) by selective catalysis of the arsenic(III) reaction. We have attempted to realize this possibility, using both potentiometric and thermometric determination of the end-point. Fairly low acid concentration is required, *i.e.*, 0·1M, as otherwise the bromide produced from the reaction of arsenic(III) with bromate, reacts with bromate after the end-point, producing bromine which initiates the oxidation of the antimony(III). We have so far been unable to find suitable conditions for this selective determination of arsenic(III), as the arsenic(V) produced reacts at least partially with antimony(III) under those conditions suitable for the selective catalysis. For the titration of arsenic(III) alone, the recommended conditions are a solution of the arsenic(III) sample in 0·1M acid (either sulphuric or hydrochloric) with one or two drops of 0·01M osmic acid catalyst added. The arsenic(III) may then by titrated directly with potassium bromate potentiometrically.

Chemistry Department
University of Strathclyde
Cathedral Street, Glasgow, C.1

D. R. Bhattarai*
J. M. Ottaway

Summary—The range of acid concentration available for the titration of arsenic(III) with bromate is considerably extended by the use of osmium tetroxide as catalyst in preference to the use of hydrochloric acid or hydrochloric acid–potassium bromide media. The acid concentration range over which reaction is stoichiometric has been established by potentiometric titration.

Zusammenfassung—Der Bereich an Säurekonzentrationen für die Titration von Arsen(III) mit Bromat läßt sich durch die Verwendung von Osmiumtetroxid als Katalysator beträchtlich ausdehnen, verglichen mit salzsauren oder salzsauren, Kalium-bromid enthaltenden Medien. Durch potentiometrische Titration wurde der Säurekonzentrationsbereich ermittelt, in dem die Reaktion stöchiometrisch abläuft.

Résumé—On étend considérablement le domaine de concentration d'acide convenable pour le dosage de l'arsenic(III) par le bromate en utilisant le tétroxyde d'osmium comme catalyseur de préférence à des milieux acide chlorhydrique ou acide chlorhydrique–bromure de potassium. On a établi le domaine de concentration d'acide dans lequel la réaction est stoechiométrique par titrage potentiométrique.

REFERENCES

1. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, Interscience, New York, 1957.
2. J. M. Ottaway and E. Bishop, *Anal. Chim. Acta* **195, 33,** 153.
3. F. E. Beamish, *The Analytical Chemistry of the Noble Metals*, Pergamon, Oxford, 1966.
4. E. Bishop, J. M. Ottaway and G. D. Short, *Anal. Chim. Acta*, 1962, **27,** 528.

---

* Present address: Nepal Geological Survey, Kathmandu, Nepal.

5. C. Surasiti and E. B. Sandell, *ibid.*, 1960, **22**, 261.
6. E. B. Sandell and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934, **56**, 1426.
7. R. L. Habig, H. L. Pardue and J. B. Worthington, *Anal. Chem.*, 1967, **39**, 600.
8. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
9. L. Szebelledy and M. Ajtai, *Mikrochem. Mikrochim. Acta*, 1938, **25**, 258; 1939, **26**, 72, 75 and 87.
10. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon, Oxford, 1966.
11. E. Bishop, in *Indicators*, Vol. 2, ed. E. Bishop, Pergamon, Oxford, 1972.
12. L. Csanji, *Acta. Chim. Acad. Sci. Hung.*, 1961, **26**, 29.

Talanta, 1972, Vol. 19, pp. 796 to 798. Pergamon Press. Printed in Northern Ireland

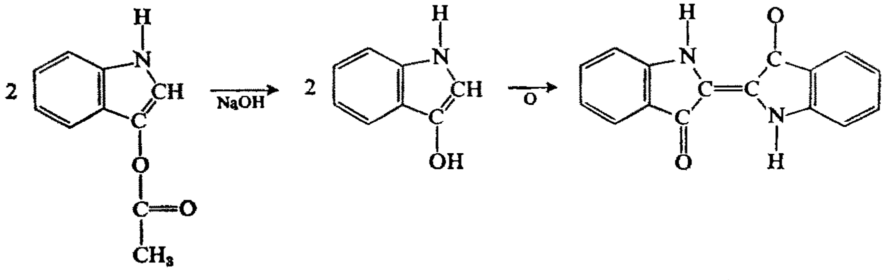
Rapid colorimetric determination of indoxyl acetate

(*Received* 31 *October* 1971. *Accepted* 3 *December* 1971)

AN ESTIMATION of cholinesterase activity can be made by following the colour or fluorescence changes produced in indoxyl acetate or other substrates.[1,2] When used to detect anticholinesterase agents, the proper colorimetric response per unit quantity of indoxyl acetate is vital, and thus a rapid method to assess the quality of each batch of recrystallized indoxyl acetate is useful. A simple colorimetric method devised for this purpose is presented here.

The determination of indoxyl (3-hydroxyindole) compounds has been widely studied as indoxyl compounds are formed by metabolic processes in the body, and certain intestinal and renal conditions are characterized by abnormally high concentrations of indoxyl and related compounds in the blood and/or urine of persons so afflicted. Several analytical methods[3-7] are routinely employed for indoxyl determination in blood or urine. These methods were generally considered too complicated for our use.

In the detection test reaction, a wetted mixture of indoxyl acetate and potassium ferricyanide reacts with acetycholinesterase to produce a blue colour when no anticholinesterase agents are present. Feigl[8] describes the similar reaction of indican, an indoxyl glucoside occurring in plants, with the enzyme emulsin. The reaction involves hydrolysis of the indican to indoxyl, which in turn is oxidized to indigo. As has been shown,[9] indoxyl compounds in urinary extracts undergo similar colour changes when treated with alkali and a mild oxidizing agent. These reactions, summarized below for indoxyl acetate, are the basis of our rapid colorimetric method.



Indoxyl acetate Indoxyl Indigo

EXPERIMENTAL

Reagents

Indoxyl acetate calibration solution. Dissolve 25 mg of recrystallized indoxyl acetate (m.p. 128° or above) in 50 ml of methanol. The solution should be freshly prepared and protected from light.

Sodium hydroxide solution, 0.1M *in methanol.*

Procedure

Prepare a solution to contain 25 mg of the indoxyl acetate to be tested, per 50 ml of methanol. Transfer 0·5 ml of this solution by Mohr pipette into a 10-ml volumetric flask, and dilute with water to approximately 9 ml. Add (Mohr pipette) 0.3 ml of methanolic 0.1M sodium hydroxide, mix, let

5. C. Surasiti and E. B. Sandell, *ibid.*, 1960, **22**, 261.
6. E. B. Sandell and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934, **56**, 1426.
7. R. L. Habig, H. L. Pardue and J. B. Worthington, *Anal. Chem.*, 1967, **39**, 600.
8. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
9. L. Szebelledy and M. Ajtai, *Mikrochem. Mikrochim. Acta*, 1938, **25**, 258; 1939, **26**, 72, 75 and 87.
10. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon, Oxford, 1966.
11. E. Bishop, in *Indicators*, Vol. 2, ed. E. Bishop, Pergamon, Oxford, 1972.
12. L. Csanji, *Acta. Chim. Acad. Sci. Hung.*, 1961, **26**, 29.

Talanta, 1972, Vol. 19, pp. 796 to 798. Pergamon Press. Printed in Northern Ireland

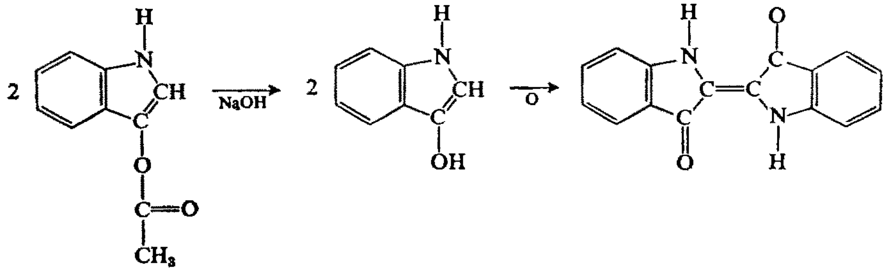
Rapid colorimetric determination of indoxyl acetate

(*Received* 31 *October* 1971. *Accepted* 3 *December* 1971)

AN ESTIMATION of cholinesterase activity can be made by following the colour or fluorescence changes produced in indoxyl acetate or other substrates.[1,2] When used to detect anticholinesterase agents, the proper colorimetric response per unit quantity of indoxyl acetate is vital, and thus a rapid method to assess the quality of each batch of recrystallized indoxyl acetate is useful. A simple colorimetric method devised for this purpose is presented here.

The determination of indoxyl (3-hydroxyindole) compounds has been widely studied as indoxyl compounds are formed by metabolic processes in the body, and certain intestinal and renal conditions are characterized by abnormally high concentrations of indoxyl and related compounds in the blood and/or urine of persons so afflicted. Several analytical methods[3–7] are routinely employed for indoxyl determination in blood or urine. These methods were generally considered too complicated for our use.

In the detection test reaction, a wetted mixture of indoxyl acetate and potassium ferricyanide reacts with acetycholinesterase to produce a blue colour when no anticholinesterase agents are present. Feigl[8] describes the similar reaction of indican, an indoxyl glucoside occurring in plants, with the enzyme emulsin. The reaction involves hydrolysis of the indican to indoxyl, which in turn is oxidized to indigo. As has been shown,[9] indoxyl compounds in urinary extracts undergo similar colour changes when treated with alkali and a mild oxidizing agent. These reactions, summarized below for indoxyl acetate, are the basis of our rapid colorimetric method.



Indoxyl acetate Indoxyl Indigo

EXPERIMENTAL

Reagents

Indoxyl acetate calibration solution. Dissolve 25 mg of recrystallized indoxyl acetate (m.p. 128° or above) in 50 ml of methanol. The solution should be freshly prepared and protected from light.

Sodium hydroxide solution, $0.1M$ in methanol.

Procedure

Prepare a solution to contain 25 mg of the indoxyl acetate to be tested, per 50 ml of methanol. Transfer 0·5 ml of this solution by Mohr pipette into a 10-ml volumetric flask, and dilute with water to approximately 9 ml. Add (Mohr pipette) 0.3 ml of methanolic $0.1M$ sodium hydroxide, mix, let stand at room temperature for 4 min and dilute to the mark with water. Read the absorbance of the blue solution *vs.* that of a reagent blank at 615 nm, in 1-cm matched cells. Find the amount of indoxyl acetate by reference to a calibration curve, or from equation (1). The indoxyl acetate batch is considered acceptable if the 0.5-ml sample taken contains 0.25 ± 0.02 mg of indoxyl acetate.

Calibration curve. Develop and measure the colour of standard solutions containing 0.2–0.6 ml of indoxyl acetate calibration solution.

RESULTS AND DISCUSSION

This procedure was developed on the basis of the results obtained during preliminary experiments described below. The addition of sodium hydroxide and an oxidant solution (potassium ferricyanide and potassium ferrocyanide) to small quantities of indoxyl acetate solution, followed by dilution, produced green rather than blue solutions. The colour was slow in forming, not intense, and unstable owing to the slow formation of a coloured precipitate. On varying the ratio of reactants, it was found that more suitable colours resulted from using less oxidant solution. This agrees with the results of staining studies(10) made with ferricyanide ions to locate indoxyl *in situ* in tissue. Elimination of the oxidant solution entirely resulted in blue reaction products, the oxidation apparently being accomplished by air. The visible absorption spectrum of the blue reaction product showed it had a broad absorption maximum in the range 600–625 nm. This range matches literature values[11] for the absorption maximum for indigo, of between 590 and 630 nm in various organic solvents.

The problem of sensitivity remained, as the colours were too light to be useful for a dependable colorimetric method. In addition, the colour development appeared to be erratic and non-reproducible. Improved results were realized when the amount of $0.1M$ sodium hydroxide added in a final reaction volume of 10 ml was limited to 0.3 ml. Other experimental variations, such as heating the test solution to 50°, using acetone or methanol as the diluent, or waiting for extended periods for full colour development, proved to be ineffective. Improved colour development, however, was later achieved by dilution of the methanolic indoxyl acetate solution with water to almost the desired volume *before* rather than *after* the addition of the 0.3 ml of sodium hydroxide solution. In this way intense and reproducible colours were fully developed after a 4-min development time at room temperature.

A calibration curve was then established for various amounts of indoxyl acetate up to 0.5 mg. The colour system obeys Beer's law in the range of 0.1–0.3 mg, and can be expressed by the relationship:

$$\text{Absorbance} = 1.94 \times \text{mg of indoxyl acetate} \tag{1}$$

The molar absorptivity at 615 nm, based on the molecular weight of indoxyl acetate, is 3720 $\text{l.mole}^{-1}.\text{cm}^{-1}$. The blue colour was found to be due to a colloidally dispersed solid, which is in agreement with the known low water-solubility of indigo. The colour, however, is stable for over 1 hr after formation. The reproducibility of the absorbance values for the colour developed for 0.25 mg of indoxyl acetate was 0.485 ± 0.005 (standard deviation) based on 8 trials. The postulated reaction of indoxyl acetate to form indigo is probably neither complete nor the only one occurring, but under the defined experimental conditions the amount of indoxyl acetate converted into indigo is apparently constant and reproducible. Because of the known composition of the samples, no study of interferences or the applicability to the determination of other indoxyl-related compounds was made. Consequently this procedure is recommended solely for the analysis of solutions containing only indoxyl acetate, although other alkali-hydrolysable indoxyl esters could probably be determined in a similar way.

Acknowledgement—This work was done under Contract DAAA 15-68-C-0675. The authors thank the Defense Development and Engineering Laboratories of Edgewood Arsenal for permission to publish this work.

Analytical Department
Westinghouse Research Laboratories
Pittsburgh, Pa. 15235, U.S.A.

R. J. NADALIN®
T. D. KACZMAREK
R. J. MCKEEVER

Summary—A rapid colorimetric method is presented for the determination of submilligram amounts of indoxyl acetate. The method depends upon the conversion of the indoxyl acetate into indigo.

Zusammenfassung—Ein schnelles kolorimetrisches Verfahren zur Bestimmung von Indoxylacetat in Mengen unter einem Milligramm wird angegeben. Es beruht auf der Umwandlung des Indoxylacetats in Indigo.

Résumé—On présente une méthode colorimétrique rapide pour le dosage de quantités à l'échelle du submilligramme d'acétate d'indoxyle. La méthode repose sur la conversion de l'acétate d'indoxyle en indigo.

REFERENCES

1. D. Kramer and R. Gamson, *Anal. Chem.*, 1957, **29**, 21A.
2. G. Guilbault and D. Kramer, *ibid.*, 1965, **37**, 120.
3. W. Fearon and J. Drum, *Sci. Proc. Royal Soc. (Dublin)*, 1951, **25**, 299; *Chem. Abstr.*, 1952, **46**, 3107.
4. A. Meiklejohn and F. Cohen, *J. Lab Clin. Med.*, 1942 **27**, 949; *Chem. Abstr.*, 1942, **36**, 3207.
5. A. Jolles, *Arch. Pharm.*, 1928, **266**, 40; *Chem. Abstr.*, 1928, **22**, 1375.
6. A. Mayer, *Nature*, 1958, **182**, 1670.
7. G. Curzon and J. Walsh, *Clin. Chem Acta*, 1962, **7**, 657.
8. F. Feigl, *Spot Tests in Organic Analysis*, 5th Ed., p. 430. Elsevier, New York, 1956.
9. E. Justin-Mueller, *J. Pharm. Chim.*, 1917, **15**, 249; *Chem. Abstr.*, 1917, **11**, 2212.
10. A. Ahlqvist, *Acta Pathol. Microbiol. Scand.*, 1960, **57**, 353; *Chem. Abstr.*, 1964, **60**, 4383.
11. *International Critical Tables*, ed. E. Washburn, National Research Council, Vol. VII, p. 203. McGraw-Hill, New York, 1930.

Talanta, 1972, Vol. 19, pp. 798 to 801. Pergamon Press. Printed in Northern Ireland

Precision of fragmentation patterns in high-resolution mass spectrometry

(*Received* 12 *October* 1971. *Accepted* 19 *November* 1971)

THE OBJECT of this work was to investigate the effect of ion-source temperature on the analytical results for high-resolution mass-spectrometric procedures. Three parameters had major effects on both absolute and relative ion intensities. These were the repeller voltage, the scan-rate and, in the case of saturated molecules, the temperature of the ion source. The work described here is concerned essentially with temperature control of the ion source and its effects on the precision of pattern coefficients and pattern summations of saturated hydrocarbon molecules.

The quantitative analysis of petroleum hydrocarbons is not widely practised at high resolution although there are many advantages in this approach. Basically, a high-resolution mass spectrometer is neither designed nor built for quantitative work. The main limitations are, of course, the effect of fast scanning (10 sec/decade) and of double-focusing the ions, both of which introduce statistical errors in measuring accurately the intensities of ions at the collector. In low-resolution work such limitations are not analytically important at slow scan-speeds (~20 min/decade).

An important criterion for the analysis of petroleum saturates has been that the ratio of the intensities of masses 127 and 226 in normal hexadecane be arbitrarily selected, along with other summations, to have certain values.[1] These values change with the source temperature—the higher the temperature the greater the fragmentation arising from the instability of the parent ions of n-hexadecane. It is necessary to know the magnitude of the effects of temperature control on both cracking patterns and summations in order to carry out quantitative high-resolution analyses of petroleum distillates.

EXPERIMENTAL

A high-resolution mass spectrometer (A.E.I. Ltd. model MS 902) was used. The associated data system MSDS-20 (and later -30), which included a DEC PDP 8i computer, automatically digitized all the ion intensities and calculated their atomic compositions. This data system was supplied with the mass spectrometer. All the results reported here were obtained with either static or dynamic resolving powers of 10,000 (~5% valley definition). High-boiling perfluorokerosene was used as an internal calibrant for the mass scale in the latter mode of operation. A standard precalibrated mass range from $m/e = 617$ to $m/e = 60$ was used in all dynamic runs.

Two different ion sources were used in the comparative studies. One was the conventional ion source with temperature not controlled; the second was a specially designed source the temperature of which was controlled (quoted as within 0.1°). Both sources and the temperature controller were supplied by A.E.I. Ltd.

The temperature in the ion source was measured with a conventional thermocouple located near the ion box. However, this recorded value, which varied with and was relative to the ambient room

5. C. Surasiti and E. B. Sandell, *ibid.*, 1960, **22**, 261.
6. E. B. Sandell and I. M. Kolthoff, *J. Am. Chem. Soc.*, 1934, **56**, 1426.
7. R. L. Habig, H. L. Pardue and J. B. Worthington, *Anal. Chem.*, 1967, **39**, 600.
8. P. A. Rodriguez and H. L. Pardue, *ibid.*, 1969, **41**, 1376.
9. L. Szebelledy and M. Ajtai, *Mikrochem. Mikrochim. Acta*, 1938, **25**, 258; 1939, **26**, 72, 75 and 87.
10. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Pergamon, Oxford, 1966.
11. E. Bishop, in *Indicators*, Vol. 2, ed. E. Bishop, Pergamon, Oxford, 1972.
12. L. Csanji, *Acta. Chim. Acad. Sci. Hung.*, 1961, **26**, 29.

Talanta, 1972, Vol. 19, pp. 796 to 798. Pergamon Press. Printed in Northern Ireland

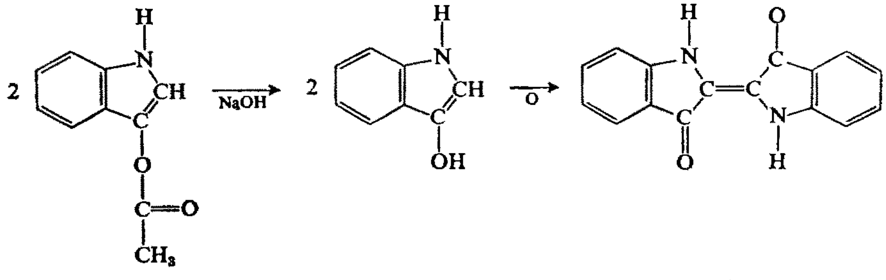
Rapid colorimetric determination of indoxyl acetate

(*Received* 31 *October* 1971. *Accepted* 3 *December* 1971)

AN ESTIMATION of cholinesterase activity can be made by following the colour or fluorescence changes produced in indoxyl acetate or other substrates.[1,2] When used to detect anticholinesterase agents, the proper colorimetric response per unit quantity of indoxyl acetate is vital, and thus a rapid method to assess the quality of each batch of recrystallized indoxyl acetate is useful. A simple colorimetric method devised for this purpose is presented here.

The determination of indoxyl (3-hydroxyindole) compounds has been widely studied as indoxyl compounds are formed by metabolic processes in the body, and certain intestinal and renal conditions are characterized by abnormally high concentrations of indoxyl and related compounds in the blood and/or urine of persons so afflicted. Several analytical methods[3-7] are routinely employed for indoxyl determination in blood or urine. These methods were generally considered too complicated for our use.

In the detection test reaction, a wetted mixture of indoxyl acetate and potassium ferricyanide reacts with acetycholinesterase to produce a blue colour when no anticholinesterase agents are present. Feigl[8] describes the similar reaction of indican, an indoxyl glucoside occurring in plants, with the enzyme emulsin. The reaction involves hydrolysis of the indican to indoxyl, which in turn is oxidized to indigo. As has been shown,[9] indoxyl compounds in urinary extracts undergo similar colour changes when treated with alkali and a mild oxidizing agent. These reactions, summarized below for indoxyl acetate, are the basis of our rapid colorimetric method.



Indoxyl acetate Indoxyl Indigo

EXPERIMENTAL

Reagents

Indoxyl acetate calibration solution. Dissolve 25 mg of recrystallized indoxyl acetate (m.p. 128° or above) in 50 ml of methanol. The solution should be freshly prepared and protected from light.

Sodium hydroxide solution, 0.1*M in methanol.*

Procedure

Prepare a solution to contain 25 mg of the indoxyl acetate to be tested, per 50 ml of methanol. Transfer 0·5 ml of this solution by Mohr pipette into a 10-ml volumetric flask, and dilute with water to approximately 9 ml. Add (Mohr pipette) 0.3 ml of methanolic 0.1*M* sodium hydroxide, mix, let stand at room temperature for 4 min and dilute to the mark with water. Read the absorbance of the blue solution *vs.* that of a reagent blank at 615 nm, in 1-cm matched cells. Find the amount of indoxyl acetate by reference to a calibration curve, or from equation (1). The indoxyl acetate batch is considered acceptable if the 0.5-ml sample taken contains 0.25 ± 0.02 mg of indoxyl acetate.

Calibration curve. Develop and measure the colour of standard solutions containing 0.2–0.6 ml of indoxyl acetate calibration solution.

RESULTS AND DISCUSSION

This procedure was developed on the basis of the results obtained during preliminary experiments described below. The addition of sodium hydroxide and an oxidant solution (potassium ferricyanide and potassium ferrocyanide) to small quantities of indoxyl acetate solution, followed by dilution, produced green rather than blue solutions. The colour was slow in forming, not intense, and unstable owing to the slow formation of a coloured precipitate. On varying the ratio of reactants, it was found that more suitable colours resulted from using less oxidant solution. This agrees with the results of staining studies(10) made with ferricyanide ions to locate indoxyl *in situ* in tissue. Elimination of the oxidant solution entirely resulted in blue reaction products, the oxidation apparently being accomplished by air. The visible absorption spectrum of the blue reaction product showed it had a broad absorption maximum in the range 600–625 nm. This range matches literature values[11] for the absorption maximum for indigo, of between 590 and 630 nm in various organic solvents.

The problem of sensitivity remained, as the colours were too light to be useful for a dependable colorimetric method. In addition, the colour development appeared to be erratic and non-reproducible. Improved results were realized when the amount of 0.1*M* sodium hydroxide added in a final reaction volume of 10 ml was limited to 0.3 ml. Other experimental variations, such as heating the test solution to 50°, using acetone or methanol as the diluent, or waiting for extended periods for full colour development, proved to be ineffective. Improved colour development, however, was later achieved by dilution of the methanolic indoxyl acetate solution with water to almost the desired volume *before* rather than *after* the addition of the 0.3 ml of sodium hydroxide solution. In this way intense and reproducible colours were fully developed after a 4-min development time at room temperature.

A calibration curve was then established for various amounts of indoxyl acetate up to 0.5 mg. The colour system obeys Beer's law in the range of 0.1–0.3 mg, and can be expressed by the relationship:

$$\text{Absorbance} = 1.94 \times \text{mg of indoxyl acetate} \tag{1}$$

The molar absorptivity at 615 nm, based on the molecular weight of indoxyl acetate, is 3720 $\text{l.mole}^{-1}.\text{cm}^{-1}$. The blue colour was found to be due to a colloidally dispersed solid, which is in agreement with the known low water-solubility of indigo. The colour, however, is stable for over 1 hr after formation. The reproducibility of the absorbance values for the colour developed for 0.25 mg of indoxyl acetate was 0.485 ± 0.005 (standard deviation) based on 8 trials. The postulated reaction of indoxyl acetate to form indigo is probably neither complete nor the only one occurring, but under the defined experimental conditions the amount of indoxyl acetate converted into indigo is apparently constant and reproducible. Because of the known composition of the samples, no study of interferences or the applicability to the determination of other indoxyl-related compounds was made. Consequently this procedure is recommended solely for the analysis of solutions containing only indoxyl acetate, although other alkali-hydrolysable indoxyl esters could probably be determined in a similar way.

Acknowledgement—This work was done under Contract DAAA 15-68-C-0675. The authors thank the Defense Development and Engineering Laboratories of Edgewood Arsenal for permission to publish this work.

Analytical Department
Westinghouse Research Laboratories
Pittsburgh, Pa. 15235, U.S.A.

R. J. NADALIN®
T. D. KACZMAREK
R. J. MCKEEVER

Summary—A rapid colorimetric method is presented for the determination of submilligram amounts of indoxyl acetate. The method depends upon the conversion of the indoxyl acetate into indigo.

Zusammenfassung—Ein schnelles kolorimetrisches Verfahren zur Bestimmung von Indoxylacetat in Mengen unter einem Milligramm wird angegeben. Es beruht auf der Umwandlung des Indoxylacetats in Indigo.

Résumé—On présente une méthode colorimétrique rapide pour le dosage de quantités à l'échelle du submilligramme d'acétate d'indoxyle. La méthode repose sur la conversion de l'acétate d'indoxyle en indigo.

REFERENCES

1. D. Kramer and R. Gamson, *Anal. Chem.*, 1957, **29**, 21A.
2. G. Guilbault and D. Kramer, *ibid.*, 1965, **37**, 120.
3. W. Fearon and J. Drum, *Sci. Proc. Royal Soc.* (*Dublin*), 1951, **25**, 299; *Chem. Abstr.*, 1952, **46**, 3107.
4. A. Meiklejohn and F. Cohen, *J. Lab Clin. Med.*, 1942 **27**, 949; *Chem. Abstr.*, 1942, **36**, 3207.
5. A. Jolles, *Arch. Pharm.*, 1928, **266**, 40; *Chem. Abstr.*, 1928, **22**, 1375.
6. A. Mayer, *Nature*, 1958, **182**, 1670.
7. G. Curzon and J. Walsh, *Clin. Chem Acta*, 1962, **7**, 657.
8. F. Feigl, *Spot Tests in Organic Analysis*, 5th Ed., p. 430. Elsevier, New York, 1956.
9. E. Justin-Mueller, *J. Pharm. Chim.*, 1917, **15**, 249; *Chem. Abstr.*, 1917, **11**, 2212.
10. A. Ahlqvist, *Acta Pathol. Microbiol. Scand.*, 1960, **57**, 353; *Chem. Abstr.*, 1964, **60**, 4383.
11. *International Critical Tables*, ed. E. Washburn, National Research Council, Vol. VII, p. 203. McGraw-Hill, New York, 1930.

Talanta, 1972, Vol. 19, pp. 798 to 801. Pergamon Press. Printed in Northern Ireland

Precision of fragmentation patterns in high-resolution mass spectrometry

(*Received* 12 *October* 1971. *Accepted* 19 *November* 1971)

THE OBJECT of this work was to investigate the effect of ion-source temperature on the analytical results for high-resolution mass-spectrometric procedures. Three parameters had major effects on both absolute and relative ion intensities. These were the repeller voltage, the scan-rate and, in the case of saturated molecules, the temperature of the ion source. The work described here is concerned essentially with temperature control of the ion source and its effects on the precision of pattern coefficients and pattern summations of saturated hydrocarbon molecules.

The quantitative analysis of petroleum hydrocarbons is not widely practised at high resolution although there are many advantages in this approach. Basically, a high-resolution mass spectrometer is neither designed nor built for quantitative work. The main limitations are, of course, the effect of fast scanning (10 sec/decade) and of double-focusing the ions, both of which introduce statistical errors in measuring accurately the intensities of ions at the collector. In low-resolution work such limitations are not analytically important at slow scan-speeds (~20 min/decade).

An important criterion for the analysis of petroleum saturates has been that the ratio of the intensities of masses 127 and 226 in normal hexadecane be arbitrarily selected, along with other summations, to have certain values.[1] These values change with the source temperature—the higher the temperature the greater the fragmentation arising from the instability of the parent ions of n-hexadecane. It is necessary to know the magnitude of the effects of temperature control on both cracking patterns and summations in order to carry out quantitative high-resolution analyses of petroleum distillates.

EXPERIMENTAL

A high-resolution mass spectrometer (A.E.I. Ltd. model MS 902) was used. The associated data system MSDS-20 (and later -30), which included a DEC PDP 8i computer, automatically digitized all the ion intensities and calculated their atomic compositions. This data system was supplied with the mass spectrometer. All the results reported here were obtained with either static or dynamic resolving powers of 10,000 (~5% valley definition). High-boiling perfluorokerosene was used as an internal calibrant for the mass scale in the latter mode of operation. A standard precalibrated mass range from $m/e = 617$ to $m/e = 60$ was used in all dynamic runs.

Two different ion sources were used in the comparative studies. One was the conventional ion source with temperature not controlled; the second was a specially designed source the temperature of which was controlled (quoted as within 0.1°). Both sources and the temperature controller were supplied by A.E.I. Ltd.

The temperature in the ion source was measured with a conventional thermocouple located near the ion box. However, this recorded value, which varied with and was relative to the ambient room

Résumé—On présente une méthode colorimétrique rapide pour le dosage de quantités à l'échelle du submilligramme d'acétate d'indoxyle. La méthode repose sur la conversion de l'acétate d'indoxyle en indigo.

REFERENCES

1. D. Kramer and R. Gamson, *Anal. Chem.*, 1957, **29**, 21A.
2. G. Guilbault and D. Kramer, *ibid.*, 1965, **37**, 120.
3. W. Fearon and J. Drum, *Sci. Proc. Royal Soc. (Dublin)*, 1951, **25**, 299; *Chem. Abstr.*, 1952, **46**, 3107.
4. A. Meiklejohn and F. Cohen, *J. Lab Clin. Med.*, 1942 **27**, 949; *Chem. Abstr.*, 1942, **36**, 3207.
5. A. Jolles, *Arch. Pharm.*, 1928, **266**, 40; *Chem. Abstr.*, 1928, **22**, 1375.
6. A. Mayer, *Nature*, 1958, **182**, 1670.
7. G. Curzon and J. Walsh, *Clin. Chem Acta*, 1962, **7**, 657.
8. F. Feigl, *Spot Tests in Organic Analysis*, 5th Ed., p. 430. Elsevier, New York, 1956.
9. E. Justin-Mueller, *J. Pharm. Chim.*, 1917, **15**, 249; *Chem. Abstr.*, 1917, **11**, 2212.
10. A. Ahlqvist, *Acta Pathol. Microbiol. Scand.*, 1960, **57**, 353; *Chem. Abstr.*, 1964, **60**, 4383.
11. *International Critical Tables*, ed. E. Washburn, National Research Council, Vol. VII, p. 203. McGraw-Hill, New York, 1930.

Talanta, 1972, Vol. 19, pp. 798 to 801. Pergamon Press. Printed in Northern Ireland

Precision of fragmentation patterns in high-resolution mass spectrometry

(*Received* 12 *October* 1971. *Accepted* 19 *November* 1971)

THE OBJECT of this work was to investigate the effect of ion-source temperature on the analytical results for high-resolution mass-spectrometric procedures. Three parameters had major effects on both absolute and relative ion intensities. These were the repeller voltage, the scan-rate and, in the case of saturated molecules, the temperature of the ion source. The work described here is concerned essentially with temperature control of the ion source and its effects on the precision of pattern coefficients and pattern summations of saturated hydrocarbon molecules.

The quantitative analysis of petroleum hydrocarbons is not widely practised at high resolution although there are many advantages in this approach. Basically, a high-resolution mass spectrometer is neither designed nor built for quantitative work. The main limitations are, of course, the effect of fast scanning (10 sec/decade) and of double-focusing the ions, both of which introduce statistical errors in measuring accurately the intensities of ions at the collector. In low-resolution work such limitations are not analytically important at slow scan-speeds (~20 min/decade).

An important criterion for the analysis of petroleum saturates has been that the ratio of the intensities of masses 127 and 226 in normal hexadecane be arbitrarily selected, along with other summations, to have certain values.[1] These values change with the source temperature—the higher the temperature the greater the fragmentation arising from the instability of the parent ions of n-hexadecane. It is necessary to know the magnitude of the effects of temperature control on both cracking patterns and summations in order to carry out quantitative high-resolution analyses of petroleum distillates.

EXPERIMENTAL

A high-resolution mass spectrometer (A.E.I. Ltd. model MS 902) was used. The associated data system MSDS-20 (and later -30), which included a DEC PDP 8i computer, automatically digitized all the ion intensities and calculated their atomic compositions. This data system was supplied with the mass spectrometer. All the results reported here were obtained with either static or dynamic resolving powers of 10,000 (~5% valley definition). High-boiling perfluorokerosene was used as an internal calibrant for the mass scale in the latter mode of operation. A standard precalibrated mass range from $m/e = 617$ to $m/e = 60$ was used in all dynamic runs.

Two different ion sources were used in the comparative studies. One was the conventional ion source with temperature not controlled; the second was a specially designed source the temperature of which was controlled (quoted as within 0.1°). Both sources and the temperature controller were supplied by A.E.I. Ltd.

The temperature in the ion source was measured with a conventional thermocouple located near the ion box. However, this recorded value, which varied with and was relative to the ambient room

temperature, gave no indication of the degree of stability afforded by the controller, which worked on an absolute basis. All the temperatures recorded in the results are therefore only approximations of the ion-source temperature.

The repeller voltage, which also affected the ion intensities, was adjusted to that value at which all peak intensities were maximized. This occurred at the first maximum of the ion repeller voltage/ion intensity curve.[3]

RESULTS

In order to isolate any effects of scan speed on the repeatability of cracking patterns, a set of data for normal hexadecane was obtained at a static resolving power of 10,000. A first set of data was recorded manually both for an uncontrolled source temperature and a controlled source temperature. A sample of normal hexadecane was vaporized in the heated inlet system (300°) and the intensities at $m/e = 226$, the parent ion, and at $m/e = 127$, a major fragment ion, were recorded over a period of 6 hr. Standard deviations for the ratio of masses 127 and 226 were computed for the mean value of the ratio for the series. Nominal temperatures of the ion source were also recorded. The results are presented in Table I. The standard deviation for the mean is considerably reduced with control of the ion-source temperature.

TABLE I.—PATTERN STABILITY FOR n-HEXADECANE AT A STATIC RESOLVING POWER OF 10000

Nominal temperature °*C*	Uncontrolled ion source temp., ratio 127/226	Nominal temperature °*C*	Controlled ion source temp. ratio 127/226
202	0·701	201	0·718
205	0·682	201	0·733
208	0·671	201	0·729
210	0·617	201	0·719
211	0·561	201	0·724
225	0·574	201	0·721
235	0·677	201	0·706
255	0·905	201	0·711
216	0·757	201	0·691
204	0·705	201	0·696
204	0·739	205	0·684
205	0·761	205	0·684
205	0·781	205	0·693
205	0·775	205	0·694
205	0·793	205	0·683
205	0·804	214	0·686
205	0·822	214	0·692
205	0·839	214	0·693
205	0·821	214	0·689
	Mean 0·7361		Mean 0·7024
	Std. devn. 0·0914;		Std. devn. 0·0167;

It is common practice to use summations of peak intensities in the analysis of petroleum, so Table II shows the stability of $\sum 71/\mathrm{TI}$ for both ion sources. Inaccuracies in $\sum 71/\mathrm{TI}$ will be ultimately reflected in any analytical results. $\sum 71$ is the sum of the C_nH_{2n+1} series *i.e.*, 71, 85, 99, 113, and TI is the sum of all the ion intensities in the spectrum. The values of $\sum 71/\mathrm{TI}$ were obtained under dynamic conditions at a scan speed of 4·6 min/decade.

The decrease in deviation is much smaller than under static conditions and the reduced deviation for the uncontrolled source is probably the result of compensating errors. Poorer ion statistics and peak clipping under dynamic conditions may partly compensate for random fluctuations of the ratio with temperature.

We found that n-$C_{16}H_{34}$ was not an ideal compound for monitoring source temperatures. We accumulated results (Table I) showing source-conditioning effects which introduced a bias into the results. To overcome this we made up a blend of paraffins (C_{10}–C_{24}) with an isomer ratio, iso/normal, of 0·5. The ion-source temperature was set to give approximately the value of the ratios suggested for performing ASTM analyses.[1] The calibration blend was run for statistical analysis and selected values of $\sum_{71}^{113} 71/\mathrm{TI}$ and 71/TI were chosen as criteria for routine operation. $\sum_{71}^{113} 71/\mathrm{TI}$ was selected

Table II.—Summed coefficients obtained for n-$C_{16}H_{34}$ at a scan speed of 4·6 min/decade and 10000 resolving power

Uncontrolled ion source temp. $\sum$ 71/TI	Controlled ion source temp. $\sum$ 71/TI
0·611	0·579
0·605	0·605
0·579	0·615
0·587	0·594
0·590	0·575
0·603	0·594
0·561	0·568
0·566	0·583
0·567	0·575
0·587	0·578
Std. devn. 0·018	Std. devn. 0·013

Table III.—Pattern stability for the calibration blend. Resolution 10000; scan rate 4·6 min/decade

$\sum$ 71/TI	71/TI
0·573	0·318
0·582	0·333
0·573	0·308
0·566	0·302
0·576	0·309
0·543	0·289
0·561	0·297
0·570	0·310
0·557	0·308
0·508	0·320
0·514	0·283
0·565	0·332
0·578	0·309
0·565	0·315
0·570	0·314
0·600	0·323
0·610	0·350
0·620	0·360
Analytical criterion 0·56 ± 0·02	Analytical criterion 0·30 ± 0·02

to be 0·56 ± 0·02 and 71/TI to be 0·30 ± 0·02. Table III shows typical results for the values of these ratios over a two-month period. The last three ratios in Table III were recorded a few days before the filament failed. The usual practice was to record the key ratios for the calibration blend and, if necessary, to adjust the source temperature to maintain the values within the stated limits. When this failed to re-establish the ratios suggested as criteria for analysis, the ion source was removed and cleaned.

DISCUSSION

The purpose of this work has been to establish the conditions for quantitative analyses at high resolution. The analysis of petroleum saturates requires constant source temperatures before meaningful analytical results are possible. The temperature stability of aromatic ions is relatively high in contrast to paraffinic ions. Since instability of paraffin ions is experimentally reflected as changes in fragmentation pattern, the overall ion stability will be related both to the ionic enthalpy

and to the value of the dissociation energy in the ion $(R_1–R_2)^+$. The ion energies are directly related to the temperature of the ion source, all other factors, such as electron energy and repeller voltage being constant. Since it is common practice to establish calibration matrices by using summations of intensities of characteristic ions, $\sum 71/TI$ for paraffins for instance, it is vital that criteria be established so that calibration and subsequent analytical results are recorded under identical conditions A calibration blend is used to check analytical results.

The effect of scan speed is also important. Scan speeds faster than 4.6 min/decade at 10,000 resolving power gave large deviations for characteristic aromatic as well as saturate summations. Under these conditions controlling the ion-source temperature to maintain precise patterns is useless, for only by increasing the number of ions collected (by larger sample size, decreased resolution and slower scan speeds) may poor ion statistics be counteracted.

Quantitative high-resolution mass spectrometry is still in its infancy and no satisfactory methods for analysing both saturates and aromatics together, by using genuine high-resolution matrices, have been published. We have found, in practice, that an adequate check on paraffin fragmentation may be maintained by running the calibration blend intermittently and recording the key intensity ratios. Small temperature variations are indicated by changes in the value of the ratios, which may be kept within the selected deviations by adjusting the source temperature. In this way it has been possible to develop methods for analysing both saturates and aromatics together and with repeatable and realistic saturate:aromatic ratios.

Gulf Oil Canada Ltd.
R and D Department
2489 North Sheridan Way
Sheridan Park, Ontario, Canada

W. F. Brown
I. P. Fisher

Summary—The effect of controlling the temperature of the ion source of a high-resolution mass spectrometer is to increase the confidence in mass spectral pattern coefficients of saturated molecules. Results are presented for both controlled and uncontrolled ion-source temperatures. Standard deviations have been calculated for selected summations of ion intensities and criteria have been suggested for maintaining meaningful analytical results in the study of petroleum distillates.

Zusammenfassung—Die Wirkung einer Temperaturregelung an der Ionenquelle eines hochauflösenden Massenspektrometers besteht in der Erhöhung der Zuverlässigkeit in den Parametern der Massenspektren gesättigter Moleküle. Ergebnisse für geregelte und nicht geregelte Temperaturen an der Ionenquelle werden mitgeteilt. Für ausgewählte Summierungen von Ionenintensitäten werden die Standardabweichungen berechnet und Kriterien vorgeschlagen, mit Hilfe derer sinnvolle analytische Ergebnisse bei der Untersuchung von Erdöldestillaten erhalten werden können.

Résumé—L'effet du contrôle de la température de la source ionique d'un spectromètre de masse à haute résolution est l'accroissement de la confiance dans les coefficients des diagrammes des spectres de masse de molécules saturées. On présente les résultats pour les températures de source ionique contrôlées et non contrôlées. On a calculé les écarts types pour des sommations choisies d'intensités d'ions et l'on suggère des critères pour conserver les résultats analytiques significatifs dans l'étude de distillats de pétrole.

REFERENCES

1. *ASTM D* 2425, 1968.
2. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, p. 105. Elsevier, London, 1960.

Talanta, 1972, Vol. 19, pp. 801 to 803. Pergamon Press. Printed in Northern Ireland

Semi-automated determination of aluminium with Xylenol Orange

(*Received* 29 *September* 1971. *Accepted* 15 *December* 1971)

Xylenol Orange has been recommended for the spectrophotometric determination of aluminium.[1–4] High sensitivity is reported. One disadvantage is the slow rate of reaction, which necessitates a

Résumé—On présente une méthode colorimétrique rapide pour le dosage de quantités à l'échelle du submilligramme d'acétate d'indoxyle. La méthode repose sur la conversion de l'acétate d'indoxyle en indigo.

REFERENCES

1. D. Kramer and R. Gamson, *Anal. Chem.*, 1957, **29**, 21A.
2. G. Guilbault and D. Kramer, *ibid.*, 1965, **37**, 120.
3. W. Fearon and J. Drum, *Sci. Proc. Royal Soc.* (*Dublin*), 1951, **25**, 299; *Chem. Abstr.*, 1952, **46**, 3107.
4. A. Meiklejohn and F. Cohen, *J. Lab Clin. Med.*, 1942 **27**, 949; *Chem. Abstr.*, 1942, **36**, 3207.
5. A. Jolles, *Arch. Pharm.*, 1928, **266**, 40; *Chem. Abstr.*, 1928, **22**, 1375.
6. A. Mayer, *Nature*, 1958, **182**, 1670.
7. G. Curzon and J. Walsh, *Clin. Chem Acta*, 1962, **7**, 657.
8. F. Feigl, *Spot Tests in Organic Analysis*, 5th Ed., p. 430. Elsevier, New York, 1956.
9. E. Justin-Mueller, *J. Pharm. Chim.*, 1917, **15**, 249; *Chem. Abstr.*, 1917, **11**, 2212.
10. A. Ahlqvist, *Acta Pathol. Microbiol. Scand.*, 1960, **57**, 353; *Chem. Abstr.*, 1964, **60**, 4383.
11. *International Critical Tables*, ed. E. Washburn, National Research Council, Vol. VII, p. 203. McGraw-Hill, New York, 1930.

Talanta, 1972, Vol. 19, pp. 798 to 801. Pergamon Press. Printed in Northern Ireland

Precision of fragmentation patterns in high-resolution mass spectrometry

(*Received* 12 *October* 1971. *Accepted* 19 *November* 1971)

THE OBJECT of this work was to investigate the effect of ion-source temperature on the analytical results for high-resolution mass-spectrometric procedures. Three parameters had major effects on both absolute and relative ion intensities. These were the repeller voltage, the scan-rate and, in the case of saturated molecules, the temperature of the ion source. The work described here is concerned essentially with temperature control of the ion source and its effects on the precision of pattern coefficients and pattern summations of saturated hydrocarbon molecules.

The quantitative analysis of petroleum hydrocarbons is not widely practised at high resolution although there are many advantages in this approach. Basically, a high-resolution mass spectrometer is neither designed nor built for quantitative work. The main limitations are, of course, the effect of fast scanning (10 sec/decade) and of double-focusing the ions, both of which introduce statistical errors in measuring accurately the intensities of ions at the collector. In low-resolution work such limitations are not analytically important at slow scan-speeds (~20 min/decade).

An important criterion for the analysis of petroleum saturates has been that the ratio of the intensities of masses 127 and 226 in normal hexadecane be arbitrarily selected, along with other summations, to have certain values.[1] These values change with the source temperature—the higher the temperature the greater the fragmentation arising from the instability of the parent ions of n-hexadecane. It is necessary to know the magnitude of the effects of temperature control on both cracking patterns and summations in order to carry out quantitative high-resolution analyses of petroleum distillates.

EXPERIMENTAL

A high-resolution mass spectrometer (A.E.I. Ltd. model MS 902) was used. The associated data system MSDS-20 (and later -30), which included a DEC PDP 8i computer, automatically digitized all the ion intensities and calculated their atomic compositions. This data system was supplied with the mass spectrometer. All the results reported here were obtained with either static or dynamic resolving powers of 10,000 (~5% valley definition). High-boiling perfluorokerosene was used as an internal calibrant for the mass scale in the latter mode of operation. A standard precalibrated mass range from $m/e = 617$ to $m/e = 60$ was used in all dynamic runs.

Two different ion sources were used in the comparative studies. One was the conventional ion source with temperature not controlled; the second was a specially designed source the temperature of which was controlled (quoted as within 0.1°). Both sources and the temperature controller were supplied by A.E.I. Ltd.

The temperature in the ion source was measured with a conventional thermocouple located near the ion box. However, this recorded value, which varied with and was relative to the ambient room

temperature, gave no indication of the degree of stability afforded by the controller, which worked on an absolute basis. All the temperatures recorded in the results are therefore only approximations of the ion-source temperature.

The repeller voltage, which also affected the ion intensities, was adjusted to that value at which all peak intensities were maximized. This occurred at the first maximum of the ion repeller voltage/ion intensity curve.[3]

RESULTS

In order to isolate any effects of scan speed on the repeatability of cracking patterns, a set of data for normal hexadecane was obtained at a static resolving power of 10,000. A first set of data was recorded manually both for an uncontrolled source temperature and a controlled source temperature. A sample of normal hexadecane was vaporized in the heated inlet system (300°) and the intensities at $m/e = 226$, the parent ion, and at $m/e = 127$, a major fragment ion, were recorded over a period of 6 hr. Standard deviations for the ratio of masses 127 and 226 were computed for the mean value of the ratio for the series. Nominal temperatures of the ion source were also recorded. The results are presented in Table I. The standard deviation for the mean is considerably reduced with control of the ion-source temperature.

TABLE I.—PATTERN STABILITY FOR n-HEXADECANE AT A STATIC RESOLVING POWER OF 10000

Nominal temperature °*C*	Uncontrolled ion source temp., ratio 127/226	Nominal temperature °*C*	Controlled ion source temp. ratio 127/226
202	0·701	201	0·718
205	0·682	201	0·733
208	0·671	201	0·729
210	0·617	201	0·719
211	0·561	201	0·724
225	0·574	201	0·721
235	0·677	201	0·706
255	0·905	201	0·711
216	0·757	201	0·691
204	0·705	201	0·696
204	0·739	205	0·684
205	0·761	205	0·684
205	0·781	205	0·693
205	0·775	205	0·694
205	0·793	205	0·683
205	0·804	214	0·686
205	0·822	214	0·692
205	0·839	214	0·693
205	0·821	214	0·689
	Mean 0·7361		Mean 0·7024
	Std. devn. 0·0914;		Std. devn. 0·0167;

It is common practice to use summations of peak intensities in the analysis of petroleum, so Table II shows the stability of $\sum 71/\mathrm{TI}$ for both ion sources. Inaccuracies in $\sum 71/\mathrm{TI}$ will be ultimately reflected in any analytical results. $\sum 71$ is the sum of the C_nH_{2n+1} series *i.e.*, 71, 85, 99, 113, and TI is the sum of all the ion intensities in the spectrum. The values of $\sum 71/\mathrm{TI}$ were obtained under dynamic conditions at a scan speed of 4·6 min/decade.

The decrease in deviation is much smaller than under static conditions and the reduced deviation for the uncontrolled source is probably the result of compensating errors. Poorer ion statistics and peak clipping under dynamic conditions may partly compensate for random fluctuations of the ratio with temperature.

We found that n-$C_{16}H_{34}$ was not an ideal compound for monitoring source temperatures. We accumulated results (Table I) showing source-conditioning effects which introduced a bias into the results. To overcome this we made up a blend of paraffins (C_{10}–C_{24}) with an isomer ratio, iso/normal, of 0·5. The ion-source temperature was set to give approximately the value of the ratios suggested for performing ASTM analyses.[1] The calibration blend was run for statistical analysis and selected values of $\sum_{71}^{113} 71/\mathrm{TI}$ and 71/TI were chosen as criteria for routine operation. $\sum_{71}^{113} 71/\mathrm{TI}$ was selected

Table II.—Summed coefficients obtained for n-$C_{16}H_{34}$ at a scan speed of 4·6 min/decade and 10000 resolving power

Uncontrolled ion source temp. $\sum$71/TI	Controlled ion source temp. $\sum$71/TI
0·611	0·579
0·605	0·605
0·579	0·615
0·587	0·594
0·590	0·575
0·603	0·594
0·561	0·568
0·566	0·583
0·567	0·575
0·587	0·578
Std. devn. 0·018	Std. devn. 0·013

Table III.—Pattern stability for the calibration blend. Resolution 10000; scan rate 4·6 min/decade

$\sum$71/TI	71/TI
0·573	0·318
0·582	0·333
0·573	0·308
0·566	0·302
0·576	0·309
0·543	0·289
0·561	0·297
0·570	0·310
0·557	0·308
0·508	0·320
0·514	0·283
0·565	0·332
0·578	0·309
0·565	0·315
0·570	0·314
0·600	0·323
0·610	0·350
0·620	0·360
Analytical criterion 0·56 ± 0·02	Analytical criterion 0·30 ± 0·02

to be 0·56 ± 0·02 and 71/TI to be 0·30 ± 0·02. Table III shows typical results for the values of these ratios over a two-month period. The last three ratios in Table III were recorded a few days before the filament failed. The usual practice was to record the key ratios for the calibration blend and, if necessary, to adjust the source temperature to maintain the values within the stated limits. When this failed to re-establish the ratios suggested as criteria for analysis, the ion source was removed and cleaned.

DISCUSSION

The purpose of this work has been to establish the conditions for quantitative analyses at high resolution. The analysis of petroleum saturates requires constant source temperatures before meaningful analytical results are possible. The temperature stability of aromatic ions is relatively high in contrast to paraffinic ions. Since instability of paraffin ions is experimentally reflected as changes in fragmentation pattern, the overall ion stability will be related both to the ionic enthalpy

and to the value of the dissociation energy in the ion $(R_1–R_2)^+$. The ion energies are directly related to the temperature of the ion source, all other factors, such as electron energy and repeller voltage being constant. Since it is common practice to establish calibration matrices by using summations of intensities of characteristic ions, $\sum 71/TI$ for paraffins for instance, it is vital that criteria be established so that calibration and subsequent analytical results are recorded under identical conditions A calibration blend is used to check analytical results.

The effect of scan speed is also important. Scan speeds faster than 4.6 min/decade at 10,000 resolving power gave large deviations for characteristic aromatic as well as saturate summations. Under these conditions controlling the ion-source temperature to maintain precise patterns is useless, for only by increasing the number of ions collected (by larger sample size, decreased resolution and slower scan speeds) may poor ion statistics be counteracted.

Quantitative high-resolution mass spectrometry is still in its infancy and no satisfactory methods for analysing both saturates and aromatics together, by using genuine high-resolution matrices, have been published. We have found, in practice, that an adequate check on paraffin fragmentation may be maintained by running the calibration blend intermittently and recording the key intensity ratios. Small temperature variations are indicated by changes in the value of the ratios, which may be kept within the selected deviations by adjusting the source temperature. In this way it has been possible to develop methods for analysing both saturates and aromatics together and with repeatable and realistic saturate: aromatic ratios.

Gulf Oil Canada Ltd.
R and D Department
2489 North Sheridan Way
Sheridan Park, Ontario, Canada

W. F. BROWN
I. P. FISHER

Summary—The effect of controlling the temperature of the ion source of a high-resolution mass spectrometer is to increase the confidence in mass spectral pattern coefficients of saturated molecules. Results are presented for both controlled and uncontrolled ion-source temperatures. Standard deviations have been calculated for selected summations of ion intensities and criteria have been suggested for maintaining meaningful analytical results in the study of petroleum distillates.

Zusammenfassung—Die Wirkung einer Temperaturregelung an der Ionenquelle eines hochauflösenden Massenspektrometers besteht in der Erhöhung der Zuverlässigkeit in den Parametern der Massenspektren gesättigter Moleküle. Ergebnisse für geregelte und nicht geregelte Temperaturen an der Ionenquelle werden mitgeteilt. Für ausgewählte Summierungen von Ionenintensitäten werden die Standardabweichungen berechnet und Kriterien vorgeschlagen, mit Hilfe derer sinnvolle analytische Ergebnisse bei der Untersuchung von Erdöldestillaten erhalten werden können.

Résumé—L'effet du contrôle de la température de la source ionique d'un spectromètre de masse à haute résolution est l'accroissement de la confiance dans les coefficients des diagrammes des spectres de masse de molécules saturées. On présente les résultats pour les températures de source ionique contrôlées et non contrôlées. On a calculé les écarts types pour des sommations choisies d'intensités d'ions et l'on suggère des critères pour conserver les résultats analytiques significatifs dans l'étude de distillats de pétrole.

REFERENCES

1. *ASTM D* 2425, 1968.
2. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, p. 105. Elsevier, London, 1960.

Talanta, 1972, Vol. 19, pp. 801 to 803. Pergamon Press. Printed in Northern Ireland

Semi-automated determination of aluminium with Xylenol Orange

(*Received* 29 *September* 1971. *Accepted* 15 *December* 1971)

XYLENOL ORANGE has been recommended for the spectrophotometric determination of aluminium.[1–4] High sensitivity is reported. One disadvantage is the slow rate of reaction, which necessitates a

and to the value of the dissociation energy in the ion $(R_1–R_2)^+$. The ion energies are directly related to the temperature of the ion source, all other factors, such as electron energy and repeller voltage being constant. Since it is common practice to establish calibration matrices by using summations of intensities of characteristic ions, $\sum 71/TI$ for paraffins for instance, it is vital that criteria be established so that calibration and subsequent analytical results are recorded under identical conditions A calibration blend is used to check analytical results.

The effect of scan speed is also important. Scan speeds faster than 4.6 min/decade at 10,000 resolving power gave large deviations for characteristic aromatic as well as saturate summations. Under these conditions controlling the ion-source temperature to maintain precise patterns is useless, for only by increasing the number of ions collected (by larger sample size, decreased resolution and slower scan speeds) may poor ion statistics be counteracted.

Quantitative high-resolution mass spectrometry is still in its infancy and no satisfactory methods for analysing both saturates and aromatics together, by using genuine high-resolution matrices, have been published. We have found, in practice, that an adequate check on paraffin fragmentation may be maintained by running the calibration blend intermittently and recording the key intensity ratios. Small temperature variations are indicated by changes in the value of the ratios, which may be kept within the selected deviations by adjusting the source temperature. In this way it has been possible to develop methods for analysing both saturates and aromatics together and with repeatable and realistic saturate:aromatic ratios.

Gulf Oil Canada Ltd.
R and D Department
2489 North Sheridan Way
Sheridan Park, Ontario, Canada

W. F. Brown
I. P. Fisher

Summary—The effect of controlling the temperature of the ion source of a high-resolution mass spectrometer is to increase the confidence in mass spectral pattern coefficients of saturated molecules. Results are presented for both controlled and uncontrolled ion-source temperatures. Standard deviations have been calculated for selected summations of ion intensities and criteria have been suggested for maintaining meaningful analytical results in the study of petroleum distillates.

Zusammenfassung—Die Wirkung einer Temperaturregelung an der Ionenquelle eines hochauflösenden Massenspektrometers besteht in der Erhöhung der Zuverlässigkeit in den Parametern der Massenspektren gesättigter Moleküle. Ergebnisse für geregelte und nicht geregelte Temperaturen an der Ionenquelle werden mitgeteilt. Für ausgewählte Summierungen von Ionenintensitäten werden die Standardabweichungen berechnet und Kriterien vorgeschlagen, mit Hilfe derer sinnvolle analytische Ergebnisse bei der Untersuchung von Erdöldestillaten erhalten werden können.

Résumé—L'effet du contrôle de la température de la source ionique d'un spectromètre de masse à haute résolution est l'accroissement de la confiance dans les coefficients des diagrammes des spectres de masse de molécules saturées. On présente les résultats pour les températures de source ionique contrôlées et non contrôlées. On a calculé les écarts types pour des sommations choisies d'intensités d'ions et l'on suggère des critères pour conserver les résultats analytiques significatifs dans l'étude de distillats de pétrole.

REFERENCES

1. *ASTM D* 2425, 1968.
2. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, p. 105. Elsevier, London, 1960.

Talanta, 1972, Vol. 19, pp. 801 to 803. Pergamon Press. Printed in Northern Ireland

Semi-automated determination of aluminium with Xylenol Orange

(*Received* 29 *September* 1971. *Accepted* 15 *December* 1971)

Xylenol Orange has been recommended for the spectrophotometric determination of aluminium.[1–4] High sensitivity is reported. One disadvantage is the slow rate of reaction, which necessitates a

heating step in the colour development. The reagent is not specific, and many elements may cause interference.[5] In most cases the interference can be eliminated by pH control, masking or extraction.

The reagent cannot be purchased in the pure state. Possible impurities include Cresol Red used in the synthesis, and another material related to Xylenol Orange and called Semi-Xylenol Orange.[6] This also forms complexes with many metals, which are indistinguishable from those of Xylenol Orange.

This report outlines the modification of the photometric method to give a semi-automated procedure using commercially available reagent in alcohol solution.

EXPERIMENTAL

Reagents

Stock solutions of Xylenol Orange ($10^{-3}M$) were prepared by dissolving the sodium salt in the minimum volume of distilled water, converting into the free acid by eluting through Zeocarb 325 (H) resin and diluting with sufficient methylated spirit to give the required concentration. The solution was standardized by photometric titration with zinc solution at pH 5·7 (hexamine buffer). The absorbance of the standardized solution was measured and allowed subsequent direct standardization by absorbance measurement.

Potassium aluminium sulphate solutions were used as calibration standards.

Equipment

A Technicon sample changer and proportioning pump were used. Colour intensity was measured by a Watson Marlow AJC automatic colorimeter with green filter number 625 (transmission maximum 25% at 531 nm). The linear output was recorded by a Heathkit servo recorder EUW 204, with 250 mV fsd.

Procedure

Two arrangements were tested, using aluminium solution in $0.1M$ acetate buffer at pH 3·8 and in $0{\cdot}05M$ sulphuric acid respectively. Pumping rates are shown in Table I.

TABLE I.—PUMPING RATE OF REAGENTS IN COLOUR DEVELOPMENT (*ml/min*)

	System *a*	System *b*
Sample	2·0	2·0
Air	0·8	0·8
$4M$ sodium acetate	—	0·1
Alcohol	1·69(s)	—
Xylenol Orange	1·69(s)	1·69(s)

(s) "Solvaflex" tubes.

System a. Reagents were mixed in a 20 × 80 × 2·5 mm coil, followed by alcohol dilution in a delay coil to increase the flow-rate in the cell. A water wash was used between samples, resulting in a small peak for the buffered solution which had zero aluminium concentration, owing to the slight colour change in the Xylenol Orange on contacting the buffer.

System b. Samples were buffered with sodium acetate in the first coil, and mixed with reagent in the second coil. A sulphuric acid wash between samples was used to avoid a colour change in the solution stream caused by the high pH of the sodium acetate.

RESULTS AND DISCUSSION

The Semi-Xylenol Orange impurity can only be removed completely with difficulty, for example by column chromatography on cellulose or multistage solvent extraction. No practical difficulties due to its presence are reported by previous authors, but there are marked differences in composition between different samples of the reagent. In the present work, no attempt was made to purify the reagent. The preparation of the solutions however confirmed the reported observation[6] that part of the Xylenol Orange is strongly adsorbed onto the cation resin, and there is an indication that the Semi-Xylenol Orange is partially removed by this process. Xylenol Orange in acid form has a single broad absorption peak, maximum 434 nm. The molar absorptivity at 434 nm, based on the standardization with zinc solution, was $1{\cdot}51 \times 10^4$ l.mole^{-1}.cm^{-1}.

The two complexes formed on reaction with aluminium and reported by previous authors are confirmed. With excess of metal ion there is a red complex, maximum absorption 555 nm, molar absorptivity $3{\cdot}16 \times 10^4$ l.mole^{-1}.cm^{-1}. With excess of reagent, a more orange complex forms, maximum absorbance about 510 nm. There is an isosbestic point at 536 nm. The molar absorptivity of the mixture at this wavelength is $1{\cdot}91 \times 10^4$ l.mole^{-1}.cm^{-4}. Measurement at this wavelength results in an indeterminate reagent blank error, but this is sufficiently small to allow linear calibration under the conditions reported.

One application of the reaction is the determination of aluminium extracted from soil samples.[3] Interference from other complexing anions is removed in the destruction of organic matter with concentrated sulphuric acid. The principal interference is from iron(III), which can be removed by preliminary extraction with cupferron from the diluted acid solution. This was found to be more satisfactory than the kinetic method previously reported. Titanium is also extracted if present, but can be stripped from the extract with ammonia solution if direct measurement of the iron cupferronate is also required. Copper and zinc form Xylenol Orange complexes of lower stability and will only interfere if present in very large excess.

Xylenol Orange has been reported to be decomposed by both ethanol and methanol.[6] In the present work, no decomposition was observed over short periods of time. Solutions were renewed if necessary after three weeks, during which time no alteration took place. After three months, notable fading of the solution had occurred, and this could be accelerated by the presence of oxidizing agents such as hydrogen peroxide or even iron(III).

In aqueous solutions Xylenol Orange reacts very slowly with aluminium at room temperature. Addition of the reagent in alcohol solution greatly increases the rate of reaction. For aluminium determination in the method under test, about equal volumes of reagent and sample were mixed. Under these conditions reaction is almost complete in 5 min, and over 70% complete in less than 1 min. This is sufficiently far advanced to permit automated colour development. A change in the total alcohol concentration has only a slight effect on the rate. Addition of alcohol to the buffered solution gave an apparent pH in the reaction mixture of 5·4–5·5, measured at the colorimeter outlet.

Each system gave a linear calibration (10 points plus zero) with aluminium concentrations from 10^{-5} to $10^{-4}M$(0–2·7μg/ml) presented at 70 samples per hour, using $1{\cdot}5 \times 10^{-4}M$ Xylenol Orange. For aluminium concentrations of less than $10^{-5}M$, the recorder scale was expanded to give 50 mV fsd and the same Xylenol Orange solution was used. More dilute Xylenol Orange solutions gave slower reaction and less reproducible results.

The repeatability of the complete process was tested with $10^{-4}M$ aluminium. The relative standard deviation on 63 results was 4·5%.

Conclusion

Xylenol Orange in alcoholic solution reacts quickly with aluminium, and is recommended for the semi-automated determination of this metal in acid solution.

Acknowledgement—The authors thank Prof. W. G. Parker and Dr. G. B. Briscoe, University of Aston in Birmingham, for the loan of some equipment used in this work.

Department of Chemistry and Metallurgy
Lanchester Polytechnic
Prioty Street, Coventry, U.K.

A. Dodson
V. J. Jennings

Summary—The photometric determination of aluminium by automated colour development with Xylenol Orange is described. The reagent has been found to act faster if used in alcohol solution.

Zusammmenfassung—Die photometrische Bestimmung von Aluminium durch automatisierte Farbentwicklung mit Xylenolorange wird beschrieben. Es wurde gefunden, daß das Reagens in alkoholischer Lösung rascher wirkt.

Résumé—On décrit le dosage photométrique de l'aluminium par révélation automatisée de la coloration avec l'Orangé Xylénol. On a trouvé que le réactif agit plus rapidement s'il est utilisé en solution alcoolique.

REFERENCES

1. M. Omoto, *Bull. Chem. Soc. Japan*, 1963, **36**, 809.
2. B. Buděšínský, *Russ. J. Anal. Chem.*, 1963, **18**, 925.
3. D. T. Pritchard, *Analyst*, 1967, **92**, 103.
4. V. A. Nazarenko and E. M. Nevskaya, *Russ. J. Anal. Chem.*, 1969, **24**, 403.
5. H. S. Flaschka and A. J. Barnard, Jr., eds, *Chelates in Analytical Chemistry*, Vol. 1, Dekker, New York, 1967.
6. M. Murakami, T. Yoshino and S. Harasawa, *Talanta*, 1967, **14**, 1293.

and to the value of the dissociation energy in the ion $(R_1-R_2)^+$. The ion energies are directly related to the temperature of the ion source, all other factors, such as electron energy and repeller voltage being constant. Since it is common practice to establish calibration matrices by using summations of intensities of characteristic ions, $\sum 71/TI$ for paraffins for instance, it is vital that criteria be established so that calibration and subsequent analytical results are recorded under identical conditions A calibration blend is used to check analytical results.

The effect of scan speed is also important. Scan speeds faster than 4.6 min/decade at 10,000 resolving power gave large deviations for characteristic aromatic as well as saturate summations. Under these conditions controlling the ion-source temperature to maintain precise patterns is useless, for only by increasing the number of ions collected (by larger sample size, decreased resolution and slower scan speeds) may poor ion statistics be counteracted.

Quantitative high-resolution mass spectrometry is still in its infancy and no satisfactory methods for analysing both saturates and aromatics together, by using genuine high-resolution matrices, have been published. We have found, in practice, that an adequate check on paraffin fragmentation may be maintained by running the calibration blend intermittently and recording the key intensity ratios. Small temperature variations are indicated by changes in the value of the ratios, which may be kept within the selected deviations by adjusting the source temperature. In this way it has been possible to develop methods for analysing both saturates and aromatics together and with repeatable and realistic saturate:aromatic ratios.

Gulf Oil Canada Ltd.
R and D Department
2489 North Sheridan Way
Sheridan Park, Ontario, Canada

W. F. Brown
I. P. Fisher

Summary—The effect of controlling the temperature of the ion source of a high-resolution mass spectrometer is to increase the confidence in mass spectral pattern coefficients of saturated molecules. Results are presented for both controlled and uncontrolled ion-source temperatures. Standard deviations have been calculated for selected summations of ion intensities and criteria have been suggested for maintaining meaningful analytical results in the study of petroleum distillates.

Zusammenfassung—Die Wirkung einer Temperaturregelung an der Ionenquelle eines hochauflösenden Massenspektrometers besteht in der Erhöhung der Zuverlässigkeit in den Parametern der Massenspektren gesättigter Moleküle. Ergebnisse für geregelte und nicht geregelte Temperaturen an der Ionenquelle werden mitgeteilt. Für ausgewählte Summierungen von Ionenintensitäten werden die Standardabweichungen berechnet und Kriterien vorgeschlagen, mit Hilfe derer sinnvolle analytische Ergebnisse bei der Untersuchung von Erdöldestillaten erhalten werden können.

Résumé—L'effet du contrôle de la température de la source ionique d'un spectromètre de masse à haute résolution est l'accroissement de la confiance dans les coefficients des diagrammes des spectres de masse de molécules saturées. On présente les résultats pour les températures de source ionique contrôlées et non contrôlées. On a calculé les écarts types pour des sommations choisies d'intensités d'ions et l'on suggère des critères pour conserver les résultats analytiques significatifs dans l'étude de distillats de pétrole.

REFERENCES

1. *ASTM D* 2425, 1968.
2. J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, p. 105. Elsevier, London, 1960.

Talanta, 1972, Vol. 19, pp. 801 to 803. Pergamon Press. Printed in Northern Ireland

Semi-automated determination of aluminium with Xylenol Orange

(*Received* 29 *September* 1971. *Accepted* 15 *December* 1971)

Xylenol Orange has been recommended for the spectrophotometric determination of aluminium.[1-4] High sensitivity is reported. One disadvantage is the slow rate of reaction, which necessitates a heating step in the colour development. The reagent is not specific, and many elements may cause interference.[5] In most cases the interference can be eliminated by pH control, masking or extraction.

The reagent cannot be purchased in the pure state. Possible impurities include Cresol Red used in the synthesis, and another material related to Xylenol Orange and called Semi-Xylenol Orange.[6] This also forms complexes with many metals, which are indistinguishable from those of Xylenol Orange.

This report outlines the modification of the photometric method to give a semi-automated procedure using commercially available reagent in alcohol solution.

EXPERIMENTAL

Reagents

Stock solutions of Xylenol Orange ($10^{-3}M$) were prepared by dissolving the sodium salt in the minimum volume of distilled water, converting into the free acid by eluting through Zeocarb 325 (H) resin and diluting with sufficient methylated spirit to give the required concentration. The solution was standardized by photometric titration with zinc solution at pH 5·7 (hexamine buffer). The absorbance of the standardized solution was measured and allowed subsequent direct standardization by absorbance measurement.

Potassium aluminium sulphate solutions were used as calibration standards.

Equipment

A Technicon sample changer and proportioning pump were used. Colour intensity was measured by a Watson Marlow AJC automatic colorimeter with green filter number 625 (transmission maximum 25% at 531 nm). The linear output was recorded by a Heathkit servo recorder EUW 204, with 250 mV fsd.

Procedure

Two arrangements were tested, using aluminium solution in 0.1*M* acetate buffer at pH 3·8 and in 0·05*M* sulphuric acid respectively. Pumping rates are shown in Table I.

TABLE I.—PUMPING RATE OF REAGENTS IN COLOUR DEVELOPMENT (*ml/min*)

	System *a*	System *b*
Sample	2·0	2·0
Air	0·8	0·8
4*M* sodium acetate	—	0·1
Alcohol	1·69(s)	—
Xylenol Orange	1·69(s)	1·69(s)

(s) "Solvaflex" tubes.

System a. Reagents were mixed in a 20 × 80 × 2·5 mm coil, followed by alcohol dilution in a delay coil to increase the flow-rate in the cell. A water wash was used between samples, resulting in a small peak for the buffered solution which had zero aluminium concentration, owing to the slight colour change in the Xylenol Orange on contacting the buffer.

System b. Samples were buffered with sodium acetate in the first coil, and mixed with reagent in the second coil. A sulphuric acid wash between samples was used to avoid a colour change in the solution stream caused by the high pH of the sodium acetate.

RESULTS AND DISCUSSION

The Semi-Xylenol Orange impurity can only be removed completely with difficulty, for example by column chromatography on cellulose or multistage solvent extraction. No practical difficulties due to its presence are reported by previous authors, but there are marked differences in composition between different samples of the reagent. In the present work, no attempt was made to purify the reagent. The preparation of the solutions however confirmed the reported observation[6] that part of the Xylenol Orange is strongly adsorbed onto the cation resin, and there is an indication that the Semi-Xylenol Orange is partially removed by this process. Xylenol Orange in acid form has a single broad absorption peak, maximum 434 nm. The molar absorptivity at 434 nm, based on the standardization with zinc solution, was $1{\cdot}51 \times 10^4$ l.mole^{-1}.cm^{-1}.

The two complexes formed on reaction with aluminium and reported by previous authors are confirmed. With excess of metal ion there is a red complex, maximum absorption 555 nm, molar absorptivity $3{\cdot}16 \times 10^4$ l.mole^{-1}.cm^{-1}. With excess of reagent, a more orange complex forms, maximum absorbance about 510 nm. There is an isosbestic point at 536 nm. The molar absorptivity of the mixture at this wavelength is $1{\cdot}91 \times 10^4$ l.mole^{-1}.cm^{-4}. Measurement at this wavelength results in an indeterminate reagent blank error, but this is sufficiently small to allow linear calibration under the conditions reported.

One application of the reaction is the determination of aluminium extracted from soil samples.[3] Interference from other complexing anions is removed in the destruction of organic matter with concentrated sulphuric acid. The principal interference is from iron(III), which can be removed by preliminary extraction with cupferron from the diluted acid solution. This was found to be more satisfactory than the kinetic method previously reported. Titanium is also extracted if present, but can be stripped from the extract with ammonia solution if direct measurement of the iron cupferronate is also required. Copper and zinc form Xylenol Orange complexes of lower stability and will only interfere if present in very large excess.

Xylenol Orange has been reported to be decomposed by both ethanol and methanol.[6] In the present work, no decomposition was observed over short periods of time. Solutions were renewed if necessary after three weeks, during which time no alteration took place. After three months, notable fading of the solution had occurred, and this could be accelerated by the presence of oxidizing agents such as hydrogen peroxide or even iron(III).

In aqueous solutions Xylenol Orange reacts very slowly with aluminium at room temperature. Addition of the reagent in alcohol solution greatly increases the rate of reaction. For aluminium determination in the method under test, about equal volumes of reagent and sample were mixed. Under these conditions reaction is almost complete in 5 min, and over 70% complete in less than 1 min. This is sufficiently far advanced to permit automated colour development. A change in the total alcohol concentration has only a slight effect on the rate. Addition of alcohol to the buffered solution gave an apparent pH in the reaction mixture of 5·4–5·5, measured at the colorimeter outlet.

Each system gave a linear calibration (10 points plus zero) with aluminium concentrations from 10^{-5} to $10^{-4}M$(0–2·7μg/ml) presented at 70 samples per hour, using $1·5 \times 10^{-4}M$ Xylenol Orange. For aluminium concentrations of less than $10^{-5}M$, the recorder scale was expanded to give 50 mV fsd and the same Xylenol Orange solution was used. More dilute Xylenol Orange solutions gave slower reaction and less reproducible results.

The repeatability of the complete process was tested with $10^{-4}M$ aluminium. The relative standard deviation on 63 results was 4·5%.

Conclusion

Xylenol Orange in alcoholic solution reacts quickly with aluminium, and is recommended for the semi-automated determination of this metal in acid solution.

Acknowledgement—The authors thank Prof. W. G. Parker and Dr. G. B. Briscoe, University of Aston in Birmingham, for the loan of some equipment used in this work.

Department of Chemistry and Metallurgy
Lanchester Polytechnic
Prioty Street, Coventry, U.K.

A. Dodson
V. J. Jennings

Summary—The photometric determination of aluminium by automated colour development with Xylenol Orange is described. The reagent has been found to act faster if used in alcohol solution.

Zusammmenfassung—Die photometrische Bestimmung von Aluminium durch automatisierte Farbentwicklung mit Xylenolorange wird beschrieben. Es wurde gefunden, daß das Reagens in alkoholischer Lösung rascher wirkt.

Résumé—On décrit le dosage photométrique de l'aluminium par révélation automatisée de la coloration avec l'Orangé Xylénol. On a trouvé que le réactif agit plus rapidement s'il est utilisé en solution alcoolique.

REFERENCES

1. M. Omoto, *Bull. Chem. Soc. Japan*, 1963, **36**, 809.
2. B. Buděšínský, *Russ. J. Anal. Chem.*, 1963, **18**, 925.
3. D. T. Pritchard, *Analyst*, 1967, **92**, 103.
4. V. A. Nazarenko and E. M. Nevskaya, *Russ. J. Anal. Chem.*, 1969, **24**, 403.
5. H. S. Flaschka and A. J. Barnard, Jr., eds, *Chelates in Analytical Chemistry*, Vol. 1, Dekker, New York, 1967.
6. M. Murakami, T. Yoshino and S. Harasawa, *Talanta*, 1967, **14**, 1293.

Talanta, 1972, Vol. 19, pp. 804 to 807. Pergamon Press. Printed in Northern Ireland

Analysis by phase-titration of three-component systems containing two mutually immiscible or partially miscible components

(*Received* 30 *August* 1971. *Accepted* 1 *November* 1971)

THE PRINCIPLE of phase-titrations has been used to determine the composition of a large number of binary solutions of organic liquids.[1-5] Suri[6] has developed a phase titration procedure for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components. The method is useful for systems where chemical determination of any of the components is difficult.

In the present communication, another phase-titration method is described, which can be used to analyse one-phase ternary mixtures containing two mutually immiscible or partially miscible components, without separate determination of any component. The method involves titrating a measured amount of the ternary mixture at constant temperature with one of the immiscible components until a second phase just appears. The refractive index (a physical property which can be quickly measured) of the resultant solution on the binodal curve is then measured, and the complete composition of the ternary mixture is calculated.

THEORY

A ternary phase-diagram for a system containing A, B and C where B and C are mutually immiscible and A is miscible with both B and C in all proportions is shown in Fig. 1. Solutions represented by a point on or below the binodal curve are heterogeneous and turbid. At constant temperature, the position of the binodal line is fixed for a given ternary mixture, and serves as a reference line in the procedure described below.

A set of binary solutions of A and B, richer in B and of known composition is prepared by weight and titrated with C until a permanent turbidity appears. The resultant ternary solution is then weighed to determine the weight of the titrant added. The turbid solution is clarified by adding a drop of two of A and the refractive index is measured. Two calibration curves are then drawn indicating (*a*) the weight of C required to produce turbidity in 1 g of the binary solution, and (*b*) the refractive index as a function of original binary composition. The procedure is repeated for binary solutions of A and C, richer in C, and another pair of calibration curves is drawn for B as the titrant.

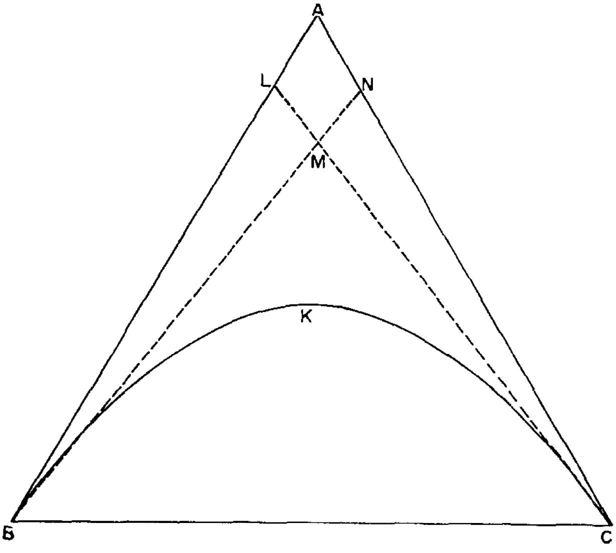


FIG. 1.—Ternary miscibility diagram showing regions suitable for phase-titration analysis.

The dual set of calibrations is necessary because sometimes only one of the two titrants will give a satisfactory end-point (see below).

To analyse a homogeneous mixture of A, B and C, two samples of known weight are titrated, one with B and the other with C to bring the composition on to the binodal curve.* The solution is weighed, clarified by adding a drop of A, and its refractive index measured.

With C used as the titrant, a refractive index value corresponding to $y\%$ B signifies the ratio of A:B in the original ternary mixture to be $(100 - y):y$ (during titration with C, the ratio remains unchanged). From the calibration curve, the weight of C required to titrate 1 g of a binary mixture of A and B in the same ratio as in the sample is found (z g). This means that $(1 + z)$ g of the turbid solution (obtained by titration with C) contains $(100 - y)/100$, $y/100$ and z g of A, B and C respectively. If x g is the weight C required to titrate 1 g of the original ternary mixture to this point on the binodal curve, the composition of the sample is given by $A = (100 - y)(1 + x)/(1 + z)\%$; $B = y(1 + x)/(1 + z)\%$, and $C = 100(z - x)/(1 + z)\%$. The calculation is similar when B is used as the titrant.

In some cases, the refractive index calibration plot show a maximum or minimum, so two composition values can correspond to a single refractive index value. To find which one refers to the actual composition, a small amount of B or C is added, the solution is clarified with A, and the direction of shift of refractive index is observed.

Ternary solutions with composition represented by a point anywhere in areas BKCL or BKCN will yield a turbidimetric end-point on titration with B and C respectively. If the composition of the ternary lies outside BKCNML, the area defined by the tangents and the binodal curve, it will not yield any turbidimetric end-point on titration with either B or C. In such cases, a sufficient and known weight of B or C is added to a known weight of the ternary, to bring its composition into one of the titratable regions BKCL or BKCN.[6]

The method is illustrated for the ternary system benzene, cyclohexane and nitromethane, the system used to illustrate the method described earlier.[6]

EXPERIMENTAL

The solvents were purified according to established procedures.[6,7] Densities and refractive index values for the liquids used are recorded in Table I along with the literature values for comparison.[8] The experimental details of the titration and the apparatus have been described earlier.[6]

Calibration curves were prepared, as outlined under *Theory*, for benzene–nitromethane mixtures titrated with cyclohexane, and for benzene–cyclohexane mixtures titrated with nitromethane. The experimental values are given in Table II.

TABLE 1.—SOME PHYSICAL PROPERTIES OF SOLVENTS USED AT 30°C

	Density, *g/ml*		Refractive index	
	Present work	Literature value[7,8]	Present work	Literature value[7,8]
Benzene	0·8685	0·8685	1·4945	1·4948
Cyclohexane	0·7694	0·7690	1·4205	1·4208*
Nitromethane	1·1239	1·1245	1·3770	1·3771*

* Values extrapolated to 30°C.

To illustrate the method, over the entire one-phase region of the system, seven synthetic ternary mixtures were prepared and analysed. The results obtained are compared with the actual composition values in Table III.

Samples 1 and 2 gave turbidimetric end-points with nitromethane, 5 and 6 with cyclohexane, 3 with both, and 4 and 7 with neither. Two sets of each of samples 4 and 7 were diluted with about the same weight of nitromethane or cyclohexane (*vide* ref. 7) and the resulting solutions titrated with cyclohexane or nitromethane respectively. The refractive indices of all the titrated solutions were measured and the weight ratios benzene:nitromethane in samples 3, 5, 6 and the solutions obtained by diluting samples 4 and 7 with nitromethane were computed from the calibration curves. The weight ratios benzene:cyclohexane in samples 1, 2, 3 and the solutions obtained by diluting samples 4 and 7 with cyclohexane were similarly calculated.

* The selection of the titrant depends on the composition of the ternary to be titrated.[5] Some samples yield turbidity with B, some with C, some with both and some with neither.[6]

TABLE II.—EXPERIMENTAL DATA FOR CALIBRATION CURVES FOR THE SYSTEM C_6H_6–C_6H_{12}–CH_3NO_2 AT 30°C.

Solutions of benzene + nitromethane titrated with cyclohexane

Weight % CH_3NO_2 in original binary	Weight of C_6H_{12} required to titrate 1 g of binary	Refractive index of the resultant solution
91·31	0·0886	1·3888
82·04	0·1336	1·4000
72·93	0·2257	1·4096
62·33	0·4200	1·4191
49·73	0·7767	1·4260

Solutions of benzene + cyclohexane titrated with nitromethane

Weight % C_6H_{12} in original binary	Weight of CH_3NO_2 required to titrate 1 g of binary	Refractive index of the resultant solution
94·18	0·0451	1·4235
83·56	0·0764	1·4293
67·69	0·2186	1·4322
59·33	0·4367	1·4308
54·06	0·6844	1·4283

TABLE III.—COMPARISON OF THE ACTUAL AND ESTIMATED COMPOSITION OF THE TERNARY MIXTURE $C_6H_6 + C_6H_{12} + CH_3NO_2$.

Sample	Cyclohexane % w/w		Nitromethene % w/w		Titrant
	Present	Estimated	Present	Estimated	
1	63·2	62·7	12·3	12·4	Nitromethane
2	52·6	52·9	13·8	13·8	Nitromethane
3	39·3	39·1	32·4	31·8	Nitromethane
		39·3		32·2	Cyclohexane
4	29·8	30·4	16·0	16·1	Nitromethane
		30·0		16·0	Cyclohexane
5	13·7	13·4	62·2	61·8	Cyclohexane
6	10·7	10·4	43·7	44·1	Cyclohexane
7	9·2	9·6	14·8	14·2	Nitromethane
		9·3		14·6	Cyclohexane

DISCUSSION

On the whole, the agreement between the actual and determined composition values (Table III) is good. The maximum difference is ~ 1% when cyclohexane is used and ~ 3% when nitromethane is used as the titrant. The agreement between the actual value and the two sets of determined values for samples 3, 4 and 7 are reasonably good.

The method of analysis is more precise and less time-consuming than the one described earlier.[6] This can be attributed to (*i*) the calibration curves being drawn directly from the experimental results and not needing any graphical treatment, and (*ii*) only one phase-titration being needed instead of the two required in the other procedure.

The procedure does not involve a separate determination of any of the components by an independent method. It is extremely useful for ternary systems where chemical analysis of any of the components is difficult. The method has, however, the same limitations and errors as other phase-titrations.[6]

Chemistry Department
Indian Institute of Technology
New Delhi-29, India

S. K. SURI

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. The method involves titrating a measured amount of the sample at constant temperature with one of the immiscible components to a turbidimetric end-point. The refractive index of the resultant solution (clarified by addition of the mutually miscible component) is determined and from the results the composition of the ternary mixture is estimated. The method is illustrated for the system consisting of benzene, cyclohexane and nitromethane.

Zusammenfassung—Beschrieben wird ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische, die zwei gegenseitig nicht mischbare oder teilweise mischbare Komponenten enthalten. Dabei wird eine abgemessene Menge der Probe bei konstanter Temperatur mit einer der nicht mischbaren Komponenten zum turbidimetrischen Endpunkt titriert. Der Brechungsindex der entstehenden Lösung (geklärt durch Zugabe der mischbaren Komponente) wird bestimmt und aus dem Ergebnis die Zusammensetzung des ternären Gemisches ermittelt. Das Verfahren wird an dem System Benzol–Cyclohexan–Nitromethan beispielhaft erläutert.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux composants non miscibles ou partiellement miscibles l'un dans l'autre. La méthode comprend le titrage à température constante d'une quantité mesurée de l'échantillon avec l'un des constituants non miscibles jusqu'à point de fin de dosage turbidimétrique. On détermine l'indice de réfraction de la solution résultante (clarifiée par addition du constituant mutuellement miscible) et l'on estime la composition du mélange ternaire à partir des résultats. La méthode est illustrée par le système constitué de benzène, cyclohexane et nitrométhane.

REFERENCES

1. C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
2. D. W. Rogers, D. L. Thompson and I. D. Chawla, *Talanta*, 1966, **13**, 1389 and references therein.
3. S. I. Spiridonova, *J. Anal. Chem.* (*U.S.S.R.*), 1949, **4**, 169 and references therein.
4. E. R. Caley and A. Habboush, *Anal. Chem.*, 1961, **33**, 1613.
5. D. A. Dunnery and G. R. Atwood, *Talanta*, 1968, **15**, 855.
6. S. K. Suri, *ibid.*, 1970, **17**, 577.
7. A. Weissberger, *Organic Solvents*, Vol. VII, 2nd Ed., Interscience, New York, 1960.
8. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.

Talanta, 1972, Vol. 19, pp. 807 to 810. Pergamon Press. Printed in Northern Ireland

Simple spectrophotometric method for determination of zirconium or hafnium in selected molybdenum-base alloys

(*Received* 13 *September* 1971. *Accepted* 2 *November* 1971)

ARSANAZO III (1,8-dihydroxynaphthalene-3,6-disulpho-2,7-bis(azo-2)-phenylarsonic acid) gives marked colour reactions with a number of elements. The high stability of the metal complexes permits the elements to be photometrically determined in strongly acidic media, which eliminates partial hydrolysis of certain elements. A high degree of selectivity is attained when determining the quadrivalent elements, zirconium and hafnium, in strongly acidic media, $9M$ hydrochloric acid.

It has been reported that no colour reactions with Arsenazo III are observed for elements having cations of radius less than 0·7–0·8 Å. The ionic radii, in Å, for those elements that might be components of molybdenum-base alloys are Cr 0·52, Fe 0·64, Mo 0·62, Ni 0·69, Re 0·56, Ta 0·68, Ti 0·68,

Talanta, 1972, Vol. 19, pp. 804 to 807. Pergamon Press. Printed in Northern Ireland

Analysis by phase-titration of three-component systems containing two mutually immiscible or partially miscible components

(*Received* 30 *August* 1971. *Accepted* 1 *November* 1971)

THE PRINCIPLE of phase-titrations has been used to determine the composition of a large number of binary solutions of organic liquids.[1-5] Suri[6] has developed a phase titration procedure for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components. The method is useful for systems where chemical determination of any of the components is difficult.

In the present communication, another phase-titration method is described, which can be used to analyse one-phase ternary mixtures containing two mutually immiscible or partially miscible components, without separate determination of any component. The method involves titrating a measured amount of the ternary mixture at constant temperature with one of the immiscible components until a second phase just appears. The refractive index (a physical property which can be quickly measured) of the resultant solution on the binodal curve is then measured, and the complete composition of the ternary mixture is calculated.

THEORY

A ternary phase-diagram for a system containing A, B and C where B and C are mutually immiscible and A is miscible with both B and C in all proportions is shown in Fig. 1. Solutions represented by a point on or below the binodal curve are heterogeneous and turbid. At constant temperature, the position of the binodal line is fixed for a given ternary mixture, and serves as a reference line in the procedure described below.

A set of binary solutions of A and B, richer in B and of known composition is prepared by weight and titrated with C until a permanent turbidity appears. The resultant ternary solution is then weighed to determine the weight of the titrant added. The turbid solution is clarified by adding a drop of two of A and the refractive index is measured. Two calibration curves are then drawn indicating (*a*) the weight of C required to produce turbidity in 1 g of the binary solution, and (*b*) the refractive index as a function of original binary composition. The procedure is repeated for binary solutions of A and C, richer in C, and another pair of calibration curves is drawn for B as the titrant.

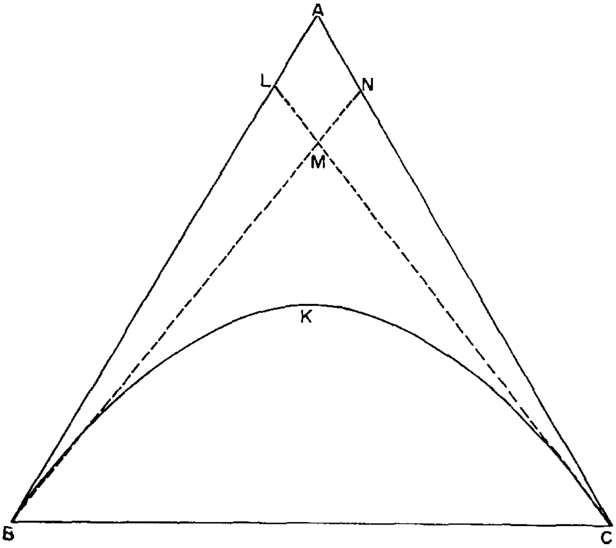


FIG. 1.—Ternary miscibility diagram showing regions suitable for phase-titration analysis.

The dual set of calibrations is necessary because sometimes only one of the two titrants will give a satisfactory end-point (see below).

To analyse a homogeneous mixture of A, B and C, two samples of known weight are titrated, one with B and the other with C to bring the composition on to the binodal curve.* The solution is weighed, clarified by adding a drop of A, and its refractive index measured.

With C used as the titrant, a refractive index value corresponding to y% B signifies the ratio of A:B in the original ternary mixture to be $(100 - y):y$ (during titration with C, the ratio remains unchanged). From the calibration curve, the weight of C required to titrate 1 g of a binary mixture of A and B in the same ratio as in the sample is found (z g). This means that $(1 + z)$ g of the turbid solution (obtained by titration with C) contains $(100 - y)/100$, $y/100$ and z g of A, B and C respectively. If x g is the weight C required to titrate 1 g of the original ternary mixture to this point on the binodal curve, the composition of the sample is given by $A = (100 - y)(1 + x)/(1 + z)\%$; $B = y(1 + x)/(1 + z)\%$, and $C = 100(z - x)/(1 + z)\%$. The calculation is similar when B is used as the titrant.

In some cases, the refractive index calibration plot show a maximum or minimum, so two composition values can correspond to a single refractive index value. To find which one refers to the actual composition, a small amount of B or C is added, the solution is clarified with A, and the direction of shift of refractive index is observed.

Ternary solutions with composition represented by a point anywhere in areas BKCL or BKCN will yield a turbidimetric end-point on titration with B and C respectively. If the composition of the ternary lies outside BKCNML, the area defined by the tangents and the binodal curve, it will not yield any turbidimetric end-point on titration with either B or C. In such cases, a sufficient and known weight of B or C is added to a known weight of the ternary, to bring its composition into one of the titratable regions BKCL or BKCN.[6]

The method is illustrated for the ternary system benzene, cyclohexane and nitromethane, the system used to illustrate the method described earlier.[6]

EXPERIMENTAL

The solvents were purified according to established procedures.[6,7] Densities and refractive index values for the liquids used are recorded in Table I along with the literature values for comparison.[8] The experimental details of the titration and the apparatus have been described earlier.[6]

Calibration curves were prepared, as outlined under *Theory*, for benzene–nitromethane mixtures titrated with cyclohexane, and for benzene–cyclohexane mixtures titrated with nitromethane. The experimental values are given in Table II.

TABLE 1.—SOME PHYSICAL PROPERTIES OF SOLVENTS USED AT 30°C

	Density, *g/ml*		Refractive index	
	Present work	Literature value[7,8]	Present work	Literature value[7,8]
Benzene	0·8685	0·8685	1·4945	1·4948
Cyclohexane	0·7694	0·7690	1·4205	1·4208*
Nitromethane	1·1239	1·1245	1·3770	1·3771*

* Values extrapolated to 30°C.

To illustrate the method, over the entire one-phase region of the system, seven synthetic ternary mixtures were prepared and analysed. The results obtained are compared with the actual composition values in Table III.

Samples 1 and 2 gave turbidimetric end-points with nitromethane, 5 and 6 with cyclohexane, 3 with both, and 4 and 7 with neither. Two sets of each of samples 4 and 7 were diluted with about the same weight of nitromethane or cyclohexane (*vide* ref. 7) and the resulting solutions titrated with cyclohexane or nitromethane respectively. The refractive indices of all the titrated solutions were measured and the weight ratios benzene:nitromethane in samples 3, 5, 6 and the solutions obtained by diluting samples 4 and 7 with nitromethane were computed from the calibration curves. The weight ratios benzene:cyclohexane in samples 1, 2, 3 and the solutions obtained by diluting samples 4 and 7 with cyclohexane were similarly calculated.

* The selection of the titrant depends on the composition of the ternary to be titrated.[5] Some samples yield turbidity with B, some with C, some with both and some with neither.[6]

TABLE II.—EXPERIMENTAL DATA FOR CALIBRATION CURVES FOR THE SYSTEM C_6H_6–C_6H_{12}–CH_3NO_2 AT 30°C.

Solutions of benzene + nitromethane titrated with cyclohexane

Weight % CH_3NO_2 in original binary	Weight of C_6H_{12} required to titrate 1 g of binary	Refractive index of the resultant solution
91·31	0·0886	1·3888
82·04	0·1336	1·4000
72·93	0·2257	1·4096
62·33	0·4200	1·4191
49·73	0·7767	1·4260

Solutions of benzene + cyclohexane titrated with nitromethane

Weight % C_6H_{12} in original binary	Weight of CH_3NO_2 required to titrate 1 g of binary	Refractive index of the resultant solution
94·18	0·0451	1·4235
83·56	0·0764	1·4293
67·69	0·2186	1·4322
59·33	0·4367	1·4308
54·06	0·6844	1·4283

TABLE III.—COMPARISON OF THE ACTUAL AND ESTIMATED COMPOSITION OF THE TERNARY MIXTURE $C_6H_6 + C_6H_{12} + CH_3NO_2$.

Sample	Cyclohexane % w/w		Nitromethene % w/w		Titrant
	Present	Estimated	Present	Estimated	
1	63·2	62·7	12·3	12·4	Nitromethane
2	52·6	52·9	13·8	13·8	Nitromethane
3	39·3	39·1	32·4	31·8	Nitromethane
		39·3		32·2	Cyclohexane
4	29·8	30·4	16·0	16·1	Nitromethane
		30·0		16·0	Cyclohexane
5	13·7	13·4	62·2	61·8	Cyclohexane
6	10·7	10·4	43·7	44·1	Cyclohexane
7	9·2	9·6	14·8	14·2	Nitromethane
		9·3		14·6	Cyclohexane

DISCUSSION

On the whole, the agreement between the actual and determined composition values (Table III) is good. The maximum difference is ~ 1% when cyclohexane is used and ~ 3% when nitromethane is used as the titrant. The agreement between the actual value and the two sets of determined values for samples 3, 4 and 7 are reasonably good.

The method of analysis is more precise and less time-consuming than the one described earlier.[6] This can be attributed to (*i*) the calibration curves being drawn directly from the experimental results and not needing any graphical treatment, and (*ii*) only one phase-titration being needed instead of the two required in the other procedure.

The procedure does not involve a separate determination of any of the components by an independent method. It is extremely useful for ternary systems where chemical analysis of any of the components is difficult. The method has, however, the same limitations and errors as other phase-titrations.[6]

Chemistry Department
Indian Institute of Technology
New Delhi-29, India

S. K. SURI

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. The method involves titrating a measured amount of the sample at constant temperature with one of the immiscible components to a turbidimetric end-point. The refractive index of the resultant solution (clarified by addition of the mutually miscible component) is determined and from the results the composition of the ternary mixture is estimated. The method is illustrated for the system consisting of benzene, cyclohexane and nitromethane.

Zusammenfassung—Beschrieben wird ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische, die zwei gegenseitig nicht mischbare oder teilweise mischbare Komponenten enthalten. Dabei wird eine abgemessene Menge der Probe bei konstanter Temperatur mit einer der nicht mischbaren Komponenten zum turbidimetrischen Endpunkt titriert. Der Brechungsindex der entstehenden Lösung (geklärt durch Zugabe der mischbaren Komponente) wird bestimmt und aus dem Ergebnis die Zusammensetzung des ternären Gemisches ermittelt. Das Verfahren wird an dem System Benzol–Cyclohexan–Nitromethan beispielhaft erläutert.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux composants non miscibles ou partiellement miscibles l'un dans l'autre. La méthode comprend le titrage à température constante d'une quantité mesurée de l'échantillon avec l'un des constituants non miscibles jusqu'à point de fin de dosage turbidimétrique. On détermine l'indice de réfraction de la solution résultante (clarifiée par addition du constituant mutuellement miscible) et l'on estime la composition du mélange ternaire à partir des résultats. La méthode est illustrée par le système constitué de benzène, cyclohexane et nitrométhane.

REFERENCES

1. C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
2. D. W. Rogers, D. L. Thompson and I. D. Chawla, *Talanta*, 1966, **13**, 1389 and references therein.
3. S. I. Spiridonova, *J. Anal. Chem.* (*U.S.S.R.*), 1949, **4**, 169 and references therein.
4. E. R. Caley and A. Habboush, *Anal. Chem.*, 1961, **33**, 1613.
5. D. A. Dunnery and G. R. Atwood, *Talanta*, 1968, **15**, 855.
6. S. K. Suri, *ibid.*, 1970, **17**, 577.
7. A. Weissberger, *Organic Solvents*, Vol. VII, 2nd Ed., Interscience, New York, 1960.
8. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.

Talanta, 1972, Vol. 19, pp. 807 to 810. Pergamon Press. Printed in Northern Ireland

Simple spectrophotometric method for determination of zirconium or hafnium in selected molybdenum-base alloys

(*Received* 13 *September* 1971. *Accepted* 2 *November* 1971)

ARSANAZO III (1,8-dihydroxynaphthalene-3,6-disulpho-2,7-bis(azo-2)-phenylarsonic acid) gives marked colour reactions with a number of elements. The high stability of the metal complexes permits the elements to be photometrically determined in strongly acidic media, which eliminates partial hydrolysis of certain elements. A high degree of selectivity is attained when determining the quadrivalent elements, zirconium and hafnium, in strongly acidic media, $9M$ hydrochloric acid.

It has been reported that no colour reactions with Arsenazo III are observed for elements having cations of radius less than 0·7–0·8 Å. The ionic radii, in Å, for those elements that might be components of molybdenum-base alloys are Cr 0·52, Fe 0·64, Mo 0·62, Ni 0·69, Re 0·56, Ta 0·68, Ti 0·68,

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. The method involves titrating a measured amount of the sample at constant temperature with one of the immiscible components to a turbidimetric end-point. The refractive index of the resultant solution (clarified by addition of the mutually miscible component) is determined and from the results the composition of the ternary mixture is estimated. The method is illustrated for the system consisting of benzene, cyclohexane and nitromethane.

Zusammenfassung—Beschrieben wird ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische, die zwei gegenseitig nicht mischbare oder teilweise mischbare Komponenten enthalten. Dabei wird eine abgemessene Menge der Probe bei konstanter Temperatur mit einer der nicht mischbaren Komponenten zum turbidimetrischen Endpunkt titriert. Der Brechungsindex der entstehenden Lösung (geklärt durch Zugabe der mischbaren Komponente) wird bestimmt und aus dem Ergebnis die Zusammensetzung des ternären Gemisches ermittelt. Das Verfahren wird an dem System Benzol–Cyclohexan–Nitromethan beispielhaft erläutert.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux composants non miscibles ou partiellement miscibles l'un dans l'autre. La méthode comprend le titrage à température constante d'une quantité mesurée de l'échantillon avec l'un des constituants non miscibles jusqu'à point de fin de dosage turbidimétrique. On détermine l'indice de réfraction de la solution résultante (clarifiée par addition du constituant mutuellement miscible) et l'on estime la composition du mélange ternaire à partir des résultats. La méthode est illustrée par le système constitué de benzène, cyclohexane et nitrométhane.

REFERENCES

1. C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
2. D. W. Rogers, D. L. Thompson and I. D. Chawla, *Talanta*, 1966, **13**, 1389 and references therein.
3. S. I. Spiridonova, *J. Anal. Chem.* (*U.S.S.R.*), 1949, **4**, 169 and references therein.
4. E. R. Caley and A. Habboush, *Anal. Chem.*, 1961, **33**, 1613.
5. D. A. Dunnery and G. R. Atwood, *Talanta*, 1968, **15**, 855.
6. S. K. Suri, *ibid.*, 1970, **17**, 577.
7. A. Weissberger, *Organic Solvents*, Vol. VII, 2nd Ed., Interscience, New York, 1960.
8. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.

Talanta, 1972, Vol. 19, pp. 807 to 810. Pergamon Press. Printed in Northern Ireland

Simple spectrophotometric method for determination of zirconium or hafnium in selected molybdenum-base alloys

(*Received* 13 *September* 1971. *Accepted* 2 *November* 1971)

ARSANAZO III (1,8-dihydroxynaphthalene-3,6-disulpho-2,7-bis(azo-2)-phenylarsonic acid) gives marked colour reactions with a number of elements. The high stability of the metal complexes permits the elements to be photometrically determined in strongly acidic media, which eliminates partial hydrolysis of certain elements. A high degree of selectivity is attained when determining the quadrivalent elements, zirconium and hafnium, in strongly acidic media, $9M$ hydrochloric acid.

It has been reported that no colour reactions with Arsenazo III are observed for elements having cations of radius less than 0·7–0·8 Å. The ionic radii, in Å, for those elements that might be components of molybdenum-base alloys are Cr 0·52, Fe 0·64, Mo 0·62, Ni 0·69, Re 0·56, Ta 0·68, Ti 0·68,

V 0·59. Zirconium has been photometrically determined in uranium with Arsenazo III. The zirconium was removed by solvent extraction before formation of the Zr–Arsenazo III complex in 6*M* hydrochloric acid. Molybdenum does not form a coloured complex with Arsenazo III, so direct photometric measurement of the Zr or Hf complex, without prior separation, was thought to be feasible.

EXPERIMENTAL

Reagents

Hydrochloric acid, conc. and 9*M*.

Nitric acid, conc.

Arsenazo III solution, 0·10%. Dissolve 100 mg of reagent in 100 ml of water containing 0·5 ml of 5% sodium carbonate solution.

Zirconium, standard solution. Dissolve 1·021 g of reactor-grade zirconium in 6*M* hydrochloric acid, with dropwise addition of the minimum of hydrofluoric acid necessary. Evaporate to dryness, then add hydrochloric acid. Repeat this twice more and finally dissolve the residue in 9*M* hydrochloric acid and dilute to 500 ml in a standard flask with that acid. Standardize by the mandelic acid method, igniting to ZrO_2. Prepare working standards by dilution with 9*M* hydrochloric acid.

Hafnium, standard solution. Oxidize 0·498 g of hafnium (99·8% pure, low zirconium content) to HfO_2 at 800°. Fuse the oxide with 2 g of sodium carbonate/sodium borate flux (1:1). Dissolve in 9*M* hydrochloric acid, transfer to a 500 ml volumetric flask and dilute to volume with 9*M* hydrochloric acid. Standardize by precipitation with mandelic acid and ignition to HfO_2. Prepare working solutions by dilution with 9*M* hydrochloric acid.

Molybdenum solution. Prepared by dissolving 2 g of molybdenum in nitric acid, and evaporating repeatedly with hydrochloric acid a minimum of three times to remove nitrate. Take up the

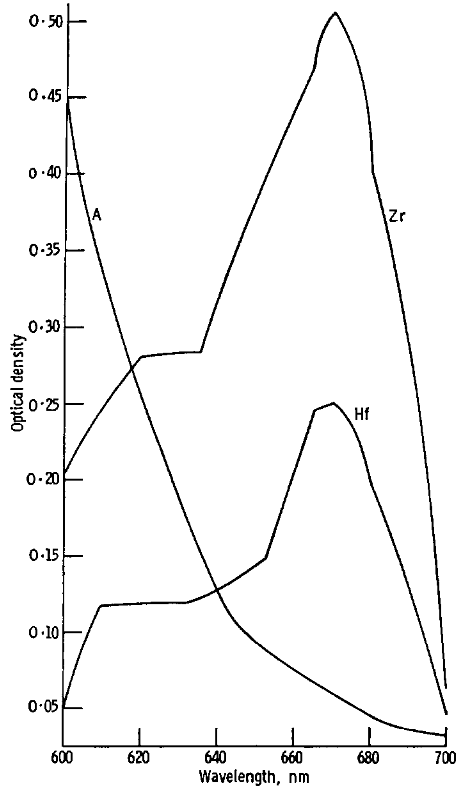


FIG. 1.—Absorption spectra of I, Zr–Arsenazo III (30 μg Zr, 4 ml g 0.01% Arsenazo III, 59 ml 9*M* hydrochloric acid; II, Hf-Arsenazo III (as for I, but 20 μg Hf instead of Zr); A, reagent blank (as for I, but without Zr).

TABLE I.—DETERMINATION OF ZIRCONIUM IN MOLYBDENUM ALLOYS

Alloy	Composition, % Ti	Zr	Re	Sample, *mg*	Zr found, %	Certificate or other value, Zr, %
TZM*	0·5	0·10	—	50	0·090‡, 0·086,‡ 0·088,§ 0·088§	
				10	0·092,‡ 0·092§	0·090*
				25	0·092,‡ 0·092§	
MoReTiZr	1·1	0·12	6·6	19	0·116, 0·116, 0·116	0·120†
				29	0·116, 0·116, 0·116	
				10	0·119, 0·119, 0·119	

* Materials Advisory Board sample and result.[8]
‡ 1-cm cell.
§ 5-cm cell.
† Gravimetric.

TABLE II.—DETERMINATION OF HAFNIUM IN MOLYBDENUM–HAFNIUM–CARBON ALLOYS

Alloy	Sample, *mg*	Hf found, %	Certificate or other value, Hf, %
MHC-20	—	0·176, 0·169	0·167*
MHC-23	—	0·760, 0·774	0·725*
MHC-24	—	1·06, 1·09	1·08*
MHC-36	4	0·312, 0·312	0·312†
	6	0·325, 0·325, 0·313, 0·313, 0·313	
	8	0·313, 0·313	
MHC-37	4	0·437, 0·437, 0·437, 0·437	0·438†
	6	0·433, 0·433, 0·425, 0·425, 0·425, 0·442, 0·442	
MHC-391	2	1·25, 1·25, 1·25, 1·30, 1·30	1·22†
	4	1·20, 1·20, 1·20, 1·27, 1·27, 1·27, 1·23, 1·23, 1·23	

* X-ray fluorescence.
† Gravimetric.

residue with 9*M* hydrochloric acid, transfer to a 200 ml volumetric flask and make up to volume with 9*M* hydrochloric acid.

Rhenium solution. Prepared by fusing 2 g of rhenium with 5 g of potassium carbonate. Dissolve the clear melt in hydrochloric acid, transfer to a 200 ml volumetric flask and make up to volume with 9*M* hydrochloric acid.

Absorption spectra The absorption spectra of Arsenazo III and its Zr and Hf complexes showed a well-defined peak at 670 nm for the complexes. The reagent had a low absorption at this wavelength (Fig. 1).

Solutions of Zr and Hf, at concentrations up to 1 µg/ml, were reacted with Arsenazo III at three hydrochloric acid concentrations, 2·76, 5·52, and 8·28*M*. The absorbances showed that sensitivity increased with hydrochloric acid concentration, and a concentration of 8.3*M* hydrochloric acid was chosen for high sensitivity.

A calibration curve was prepared, standard Zr solution being added to a 50-ml volumetric flask containing 25 ml of 9*M* hydrochloric acid, followed by addition of 4 ml of Arsenazo III solution and dilution to 50 ml with the acid. The absorbance was measured at 670 nm in a 1-cm cell and corrected for the blank. Beer's law was obeyed up to 20 µg of zirconium. Addition of 10 mg of molybdenum, 10 mg of rhenium, or 1 mg of titanium did not affect the calibration curve.

Calibration curves for 10 µg of zirconium in 50 ml of final solution, similarly prepared, were equally satisfactory, either 2-cm or 5-cm cells being used.

Similar results were obtained for hafnium by the same procedure, for the 0–50 and 0–10 µg ranges.

Procedure

Weigh a sample of a size based on the expected homogeneity of the alloy, place it in a 250-ml beaker, dissolve it in *aqua regia*, then remove the cover glass and evaporate to dryness under infrared drying lamps. Cool, add 20 ml of conc. hydrochloric acid, rinse down the sides of the beaker and again evaporate to dryness under the lamps. Repeat this operation at least twice more for the complete removal of nitrate. Cool, add 20–30 ml of $9M$ hydrochloric acid to dissolve the metal salts, transfer the sample solution to a suitable volumetric flask, dilute to volume with $9M$ hydrochloric acid and mix thoroughly. Transfer a suitable aliquot containing not more than 20 μg of zirconium or 50 μg of hafnium to a 50 ml volumetric flask containing 25 ml of $9M$ hydrochloric acid. Prepare a similar reagent blank. Add 4 ml of Arsenazo III solution to each flask, dilute to volume with $9M$ hydrochloric acid, mix, measure the absorbance for samples and the blank. Apply the blank correction.

RESULTS

The procedure was applied to four molybdenum alloys, with the results shown in Tables I and II. The results show good agreement with accepted values, and are reproducible. The method is simple and no prior separation is necessary. The relative standard deviation ranges from 1·3 to 2·7%.

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135, *U.S.A.*

William A. Dupraw

Summary—A simple analytical procedure is described for determining zirconium or hafnium in molybdenum-base alloys by formation of the Arsenazo III complex of zirconium or hafnium in $9M$ hydrochloric acid medium. The absorbance is measured at 670 nm. Molybdenum (10 mg), titanium (1 mg), and rhenium (10 mg) have no adverse effect. No prior separation is needed. The relative standard deviation is 1·3–2·7%.

Zusammenfassung—Ein einfaches analytisches Verfahren zur Bestimmung von Zirkonium oder Hafnium in Legierungen auf Molybdängrundlage wird beschrieben. Es beruht auf der Bildung des Komplexes von Zirkonium oder Hafnium mit Arsenazo III in 9 M Salzsäure. Die Extinktion wird bei 670 nm gemessen. 10 mg Molybdän, 1 mg Titan und 10 mg Rhenium stören nicht. Es ist keine vorhergehende Abtrennung notwendig. Die relative Standardabweichung betragt 1,3–2,7%.

Résumé—On décrit une technique analytique simple pour le dosage du zirconium ou du hafnium dans les alliages à base de molybdène par formation du complexe Arsenazo III du zirconium ou du hafnium en milieu acide chlorhydrique $9M$. On mesure l'absorption à 670 nm. Le molybdène (10 mg), le titane (1 mg) et le rhénium (10 mg) n'ont pas d'effet défavorable. Une séparation préalable n'est pas nécessaire. L'écart type relatif est 1,3–2,7%.

REFERENCES

1. S. B. Savvin, *Talanta*, 1964, **11**, 7.
2. O. A. Vita, *Goodyear Atomic Corporation Report* GAT-524, 1966.
3. D. L. Chase, *Battelle Memorial Institute DMIC Report* 220, 1965.

Talanta, 1972, Vol. 19, pp. 810 to 814. Pergamon Press. Printed in Northern Ireland

Qualitative identification of alloys by energy-dispersive X-ray spectroscopy*

(*Received* 23 *September* 1971. *Accepted* 14 *November* 1971)

ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDXS) has been advancing rapidly in recent years, largely on account of the development of high-resolution semiconductor detectors and the increasing availability of radioisotopic sources suitable for use in excitation. The use of this technique for quantitative

* This work was supported by the United States Atomic Energy Commission.

Summary—A method, based on phase titration, for the analysis of ternary mixtures containing two mutually immiscible or partially miscible components is described. The method involves titrating a measured amount of the sample at constant temperature with one of the immiscible components to a turbidimetric end-point. The refractive index of the resultant solution (clarified by addition of the mutually miscible component) is determined and from the results the composition of the ternary mixture is estimated. The method is illustrated for the system consisting of benzene, cyclohexane and nitromethane.

Zusammenfassung—Beschrieben wird ein auf einer Phasentitration beruhendes Verfahren zur Analyse ternärer Gemische, die zwei gegenseitig nicht mischbare oder teilweise mischbare Komponenten enthalten. Dabei wird eine abgemessene Menge der Probe bei konstanter Temperatur mit einer der nicht mischbaren Komponenten zum turbidimetrischen Endpunkt titriert. Der Brechungsindex der entstehenden Lösung (geklärt durch Zugabe der mischbaren Komponente) wird bestimmt und aus dem Ergebnis die Zusammensetzung des ternären Gemisches ermittelt. Das Verfahren wird an dem System Benzol–Cyclohexan–Nitromethan beispielhaft erläutert.

Résumé—On décrit une méthode basée sur le titrage de phase pour l'analyse de mélanges ternaires contenant deux composants non miscibles ou partiellement miscibles l'un dans l'autre. La méthode comprend le titrage à température constante d'une quantité mesurée de l'échantillon avec l'un des constituants non miscibles jusqu'à point de fin de dosage turbidimétrique. On détermine l'indice de réfraction de la solution résultante (clarifiée par addition du constituant mutuellement miscible) et l'on estime la composition du mélange ternaire à partir des résultats. La méthode est illustrée par le système constitué de benzène, cyclohexane et nitrométhane.

REFERENCES

1. C. D. Bogin, *Ind. Eng. Chem.*, 1924, **16**, 380.
2. D. W. Rogers, D. L. Thompson and I. D. Chawla, *Talanta*, 1966, **13**, 1389 and references therein.
3. S. I. Spiridonova, *J. Anal. Chem.* (*U.S.S.R.*), 1949, **4**, 169 and references therein.
4. E. R. Caley and A. Habboush, *Anal. Chem.*, 1961, **33**, 1613.
5. D. A. Dunnery and G. R. Atwood, *Talanta*, 1968, **15**, 855.
6. S. K. Suri, *ibid.*, 1970, **17**, 577.
7. A. Weissberger, *Organic Solvents*, Vol. VII, 2nd Ed., Interscience, New York, 1960.
8. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier, Amsterdam, 1950.

Talanta, 1972, Vol. 19, pp. 807 to 810. Pergamon Press. Printed in Northern Ireland

Simple spectrophotometric method for determination of zirconium or hafnium in selected molybdenum-base alloys

(*Received* 13 *September* 1971. *Accepted* 2 *November* 1971)

ARSANAZO III (1,8-dihydroxynaphthalene-3,6-disulpho-2,7-bis(azo-2)-phenylarsonic acid) gives marked colour reactions with a number of elements. The high stability of the metal complexes permits the elements to be photometrically determined in strongly acidic media, which eliminates partial hydrolysis of certain elements. A high degree of selectivity is attained when determining the quadrivalent elements, zirconium and hafnium, in strongly acidic media, $9M$ hydrochloric acid.

It has been reported that no colour reactions with Arsenazo III are observed for elements having cations of radius less than 0·7–0·8 Å. The ionic radii, in Å, for those elements that might be components of molybdenum-base alloys are Cr 0·52, Fe 0·64, Mo 0·62, Ni 0·69, Re 0·56, Ta 0·68, Ti 0·68,

V 0·59. Zirconium has been photometrically determined in uranium with Arsenazo III. The zirconium was removed by solvent extraction before formation of the Zr–Arsenazo III complex in 6*M* hydrochloric acid. Molybdenum does not form a coloured complex with Arsenazo III, so direct photometric measurement of the Zr or Hf complex, without prior separation, was thought to be feasible.

EXPERIMENTAL

Reagents

Hydrochloric acid, conc. and 9*M*.

Nitric acid, conc.

Arsenazo III solution, 0·10%. Dissolve 100 mg of reagent in 100 ml of water containing 0·5 ml of 5% sodium carbonate solution.

Zirconium, standard solution. Dissolve 1·021 g of reactor-grade zirconium in 6*M* hydrochloric acid, with dropwise addition of the minimum of hydrofluoric acid necessary. Evaporate to dryness, then add hydrochloric acid. Repeat this twice more and finally dissolve the residue in 9*M* hydrochloric acid and dilute to 500 ml in a standard flask with that acid. Standardize by the mandelic acid method, igniting to ZrO_2. Prepare working standards by dilution with 9*M* hydrochloric acid.

Hafnium, standard solution. Oxidize 0·498 g of hafnium (99·8% pure, low zirconium content) to HfO_2 at 800°. Fuse the oxide with 2 g of sodium carbonate/sodium borate flux (1 :1). Dissolve in 9*M* hydrochloric acid, transfer to a 500 ml volumetric flask and dilute to volume with 9*M* hydrochloric acid. Standardize by precipitation with mandelic acid and ignition to HfO_2. Prepare working solutions by dilution with 9*M* hydrochloric acid.

Molybdenum solution. Prepared by dissolving 2 g of molybdenum in nitric acid, and evaporating repeatedly with hydrochloric acid a minimum of three times to remove nitrate. Take up the

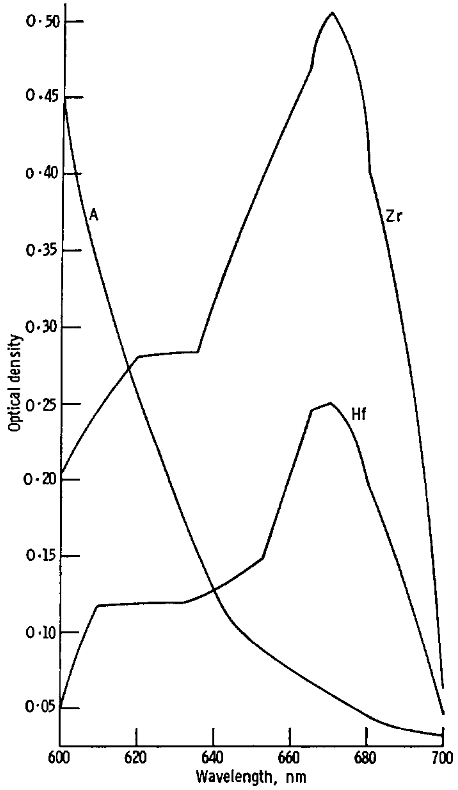


FIG. 1.—Absorption spectra of I, Zr–Arsenazo III (30 μg Zr, 4 ml g 0.01% Arsenazo III, 59 ml 9*M* hydrochloric acid; II, Hf-Arsenazo III (as for I, but 20 μg Hf instead of Zr); A, reagent blank (as for I, but without Zr).

Table I.—Determination of zirconium in molybdenum alloys

Alloy	Composition, %			Sample, *mg*	Zr found, %	Certificate or other value, Zr, %
	Ti	Zr	Re			
TZM*	0·5	0·10	—	50	0·090‡, 0·086,‡ 0·088,§ 0·088§	
				10	0·092,‡ 0·092§	0·090*
				25	0·092,‡ 0·092§	
MoReTiZr	1·1	0·12	6·6	19	0·116, 0·116, 0·116	0·120†
				29	0·116, 0·116, 0·116	
				10	0·119, 0·119, 0·119	

* Materials Advisory Board sample and result.[8]
‡ 1-cm cell.
§ 5-cm cell.
† Gravimetric.

Table II.—Determination of hafnium in molybdenum–hafnium–carbon alloys

Alloy	Sample, *mg*	Hf found, %	Certificate or other value, Hf, %
MHC-20	—	0·176, 0·169	0·167*
MHC-23	—	0·760, 0·774	0·725*
MHC-24	—	1·06, 1·09	1·08*
MHC-36	4	0·312, 0·312	0·312†
	6	0·325, 0·325, 0·313, 0·313, 0·313	
	8	0·313, 0·313	
MHC-37	4	0·437, 0·437, 0·437, 0·437	0·438†
	6	0·433, 0·433, 0·425, 0·425, 0·425, 0·442, 0·442	
MHC-391	2	1·25, 1·25, 1·25, 1·30, 1·30	1·22†
	4	1·20, 1·20, 1·20, 1·27, 1·27, 1·27, 1·23, 1·23, 1·23	

* X-ray fluorescence.
† Gravimetric.

residue with 9*M* hydrochloric acid, transfer to a 200 ml volumetric flask and make up to volume with 9*M* hydrochloric acid.

Rhenium solution. Prepared by fusing 2 g of rhenium with 5 g of potassium carbonate. Dissolve the clear melt in hydrochloric acid, transfer to a 200 ml volumetric flask and make up to volume with 9*M* hydrochloric acid.

Absorption spectra The absorption spectra of Arsenazo III and its Zr and Hf complexes showed a well-defined peak at 670 nm for the complexes. The reagent had a low absorption at this wavelength (Fig. 1).

Solutions of Zr and Hf, at concentrations up to 1 μg/ml, were reacted with Arsenazo III at three hydrochloric acid concentrations, 2·76, 5·52, and 8·28*M*. The absorbances showed that sensitivity increased with hydrochloric acid concentration, and a concentration of 8.3*M* hydrochloric acid was chosen for high sensitivity.

A calibration curve was prepared, standard Zr solution being added to a 50-ml volumetric flask containing 25 ml of 9*M* hydrochloric acid, followed by addition of 4 ml of Arsenazo III solution and dilution to 50 ml with the acid. The absorbance was measured at 670 nm in a 1-cm cell and corrected for the blank. Beer's law was obeyed up to 20 μg of zirconium. Addition of 10 mg of molybdenum, 10 mg of rhenium, or 1 mg of titanium did not affect the calibration curve.

Calibration curves for 10 μg of zirconium in 50 ml of final solution, similarly prepared, were equally satisfactory, either 2-cm or 5-cm cells being used.

Similar results were obtained for hafnium by the same procedure, for the 0–50 and 0–10 μg ranges.

Procedure

Weigh a sample of a size based on the expected homogeneity of the alloy, place it in a 250-ml beaker, dissolve it in *aqua regia*, then remove the cover glass and evaporate to dryness under infrared drying lamps. Cool, add 20 ml of conc. hydrochloric acid, rinse down the sides of the beaker and again evaporate to dryness under the lamps. Repeat this operation at least twice more for the complete removal of nitrate. Cool, add 20–30 ml of $9M$ hydrochloric acid to dissolve the metal salts, transfer the sample solution to a suitable volumetric flask, dilute to volume with $9M$ hydrochloric acid and mix thoroughly. Transfer a suitable aliquot containing not more than 20 μg of zirconium or 50 μg of hafnium to a 50 ml volumetric flask containing 25 ml of $9M$ hydrochloric acid. Prepare a similar reagent blank. Add 4 ml of Arsenazo III solution to each flask, dilute to volume with $9M$ hydrochloric acid, mix, measure the absorbance for samples and the blank. Apply the blank correction.

RESULTS

The procedure was applied to four molybdenum alloys, with the results shown in Tables I and II. The results show good agreement with accepted values, and are reproducible. The method is simple and no prior separation is necessary. The relative standard deviation ranges from 1·3 to 2·7%.

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135, *U.S.A.*

William A. Dupraw

Summary—A simple analytical procedure is described for determining zirconium or hafnium in molybdenum-base alloys by formation of the Arsenazo III complex of zirconium or hafnium in $9M$ hydrochloric acid medium. The absorbance is measured at 670 nm. Molybdenum (10 mg), titanium (1 mg), and rhenium (10 mg) have no adverse effect. No prior separation is needed. The relative standard deviation is 1·3–2·7%.

Zusammenfassung—Ein einfaches analytisches Verfahren zur Bestimmung von Zirkonium oder Hafnium in Legierungen auf Molybdängrundlage wird beschrieben. Es beruht auf der Bildung des Komplexes von Zirkonium oder Hafnium mit Arsenazo III in 9 M Salzsäure. Die Extinktion wird bei 670 nm gemessen. 10 mg Molybdän, 1 mg Titan und 10 mg Rhenium stören nicht. Es ist keine vorhergehende Abtrennung notwendig. Die relative Standardabweichung betragt 1,3–2,7%.

Résumé—On décrit une technique analytique simple pour le dosage du zirconium ou du hafnium dans les alliages à base de molybdène par formation du complexe Arsenazo III du zirconium ou du hafnium en milieu acide chlorhydrique $9M$. On mesure l'absorption à 670 nm. Le molybdène (10 mg), le titane (1 mg) et le rhénium (10 mg) n'ont pas d'effet défavorable. Une séparation préalable n'est pas nécessaire. L'écart type relatif est 1,3–2,7%.

REFERENCES

1. S. B. Savvin, *Talanta*, 1964, **11**, 7.
2. O. A. Vita, *Goodyear Atomic Corporation Report* GAT-524, 1966.
3. D. L. Chase, *Battelle Memorial Institute DMIC Report* 220, 1965.

Talanta, 1972, Vol. 19, pp. 810 to 814. Pergamon Press. Printed in Northern Ireland

Qualitative identification of alloys by energy-dispersive X-ray spectroscopy*

(*Received* 23 *September* 1971. *Accepted* 14 *November* 1971)

Energy-dispersive X-ray spectroscopy (EDXS) has been advancing rapidly in recent years, largely on account of the development of high-resolution semiconductor detectors and the increasing availability of radioisotopic sources suitable for use in excitation. The use of this technique for quantitative

---

* This work was supported by the United States Atomic Energy Commission.

Procedure

Weigh a sample of a size based on the expected homogeneity of the alloy, place it in a 250-ml beaker, dissolve it in *aqua regia*, then remove the cover glass and evaporate to dryness under infrared drying lamps. Cool, add 20 ml of conc. hydrochloric acid, rinse down the sides of the beaker and again evaporate to dryness under the lamps. Repeat this operation at least twice more for the complete removal of nitrate. Cool, add 20–30 ml of $9M$ hydrochloric acid to dissolve the metal salts, transfer the sample solution to a suitable volumetric flask, dilute to volume with $9M$ hydrochloric acid and mix thoroughly. Transfer a suitable aliquot containing not more than 20 μg of zirconium or 50 μg of hafnium to a 50 ml volumetric flask containing 25 ml of $9M$ hydrochloric acid. Prepare a similar reagent blank. Add 4 ml of Arsenazo III solution to each flask, dilute to volume with $9M$ hydrochloric acid, mix, measure the absorbance for samples and the blank. Apply the blank correction.

RESULTS

The procedure was applied to four molybdenum alloys, with the results shown in Tables I and II. The results show good agreement with accepted values, and are reproducible. The method is simple and no prior separation is necessary. The relative standard deviation ranges from 1·3 to 2·7%.

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135, *U.S.A.*

William A. Dupraw

Summary—A simple analytical procedure is described for determining zirconium or hafnium in molybdenum-base alloys by formation of the Arsenazo III complex of zirconium or hafnium in $9M$ hydrochloric acid medium. The absorbance is measured at 670 nm. Molybdenum (10 mg), titanium (1 mg), and rhenium (10 mg) have no adverse effect. No prior separation is needed. The relative standard deviation is 1·3–2·7%.

Zusammenfassung—Ein einfaches analytisches Verfahren zur Bestimmung von Zirkonium oder Hafnium in Legierungen auf Molybdängrundlage wird beschrieben. Es beruht auf der Bildung des Komplexes von Zirkonium oder Hafnium mit Arsenazo III in 9 M Salzsäure. Die Extinktion wird bei 670 nm gemessen. 10 mg Molybdän, 1 mg Titan und 10 mg Rhenium stören nicht. Es ist keine vorhergehende Abtrennung notwendig. Die relative Standardabweichung betragt 1,3–2,7%.

Résumé—On décrit une technique analytique simple pour le dosage du zirconium ou du hafnium dans les alliages à base de molybdène par formation du complexe Arsenazo III du zirconium ou du hafnium en milieu acide chlorhydrique $9M$. On mesure l'absorption à 670 nm. Le molybdène (10 mg), le titane (1 mg) et le rhénium (10 mg) n'ont pas d'effet défavorable. Une séparation préalable n'est pas nécessaire. L'écart type relatif est 1,3–2,7%.

REFERENCES

1. S. B. Savvin, *Talanta*, 1964, **11**, 7.
2. O. A. Vita, *Goodyear Atomic Corporation Report* GAT-524, 1966.
3. D. L. Chase, *Battelle Memorial Institute DMIC Report* 220, 1965.

Talanta, 1972, Vol. 19, pp. 810 to 814. Pergamon Press. Printed in Northern Ireland

Qualitative identification of alloys by energy-dispersive X-ray spectroscopy*

(*Received* 23 *September* 1971. *Accepted* 14 *November* 1971)

Energy-dispersive X-ray spectroscopy (EDXS) has been advancing rapidly in recent years, largely on account of the development of high-resolution semiconductor detectors and the increasing availability of radioisotopic sources suitable for use in excitation. The use of this technique for quantitative

---

* This work was supported by the United States Atomic Energy Commission.

analysis involves inherent difficulties, one of the main problems being differences in matrix effects when samples and standards are not identical in chemical and physical characteristics. However, there are means whereby these problems may be minimized.[1–5] The literature contains numerous papers[6–12] on the technique, the application to quantitative analyses, and descriptions of radioisotope source assemblies. Therefore, the theory of the method and the varied applications will not be presented here.

The application of EDXS to qualitative analysis is relatively rapid and generally straightforward. The $K\alpha$ and $K\beta$ or $L\alpha$, $L\beta$, and $L\gamma$ peaks obtained experimentally can be compared with the corresponding peaks obtained from standards or with tabulated values, to obtain qualitative identification. By use of a source which emits photons with a definite maximum energy, either in the form of X-rays, gamma-rays or bremsstrahlung, the range of elements which can be excited and caused to emit characteristic X-rays can be controlled. There are a number of commercially available radioisotopic sources and required sources that are not available can be prepared. The sensitivity, which is dependent on a number of parameters such as matrix, atomic number and excitation source, is in the range from parts per thousand to parts per million for most elements. For $18 > Z > 10$, the use of helium or vacuum, rather than air, in the apparatus is necessary. Elements with $Z < 10$ are not directly detectable by this technique.

In an analytical laboratory, the use of EDXS for qualitative analysis can relieve the sample load on other methods such as emission spectroscopy. Since these other techniques are capable of identifying specific alloys, full utilization of EDXS should include qualitative identification of alloys.

Although Sellers and Brinkerhoff[12] have suggested a technique for alloy sorting which uses energy filters and multiple counts, the method described in this paper requires only one sample counting and no filters are needed. The experimental results are incorporated with specification data in a graph which permits unique identification of a specific alloy within an alloy type.

EXPERIMENTAL

Instrumentation

A Nuclear Diodes EDXS system, Model XS-25-240-DSS, was used in this work. The Si(Li) detector was 25 mm^2 × 3 mm and had a 2-mil beryllium window. The signals were passed through an amplifier into a TMC 404C analyser. The system resolution was <300 eV FWHM (full peak width at half the maximum peak height) for the 6·4 keV $K\alpha$ X-rays of iron.

Samples were supported on a Mylar film stretched across a Nuclear Diodes Model XFS-1 source-holder. The sources were mounted in the holder such that line of sight between the source and sample was at 45° to the axis defined by the sample and detector. The holder shielded the detector from direct bombardment by the source and also served to collimate the X-rays generated in the sample.

Excitation

Samples were placed by hand in the centre of the Mylar film as reproducibly as possible. ^{241}Am and ^{109}Cd sources were used individually for excitation of the characteristic X-ray lines of the samples. Accumulation of the spectra was for either 1 or 4 min, depending on the size of the samples and the intensity of the X-rays produced. The areas under the individual peaks of interest were obtained by integration with a TMC Resolver/Integrator unit.

Samples

The samples used in this work were NBS SRM brass standards (standards C1103–C1119), lead–tin solder spectrochemical standards obtained from Morris P. Kirk Co. (standard numbers 527–585), analysed stainless steel (austenitic) from Armco Steel Co., Rustless Division and a gold–silver alloy series prepared in this laboratory and analysed by standard wet chemical procedures.

RESULTS AND DISCUSSION

In the case of the brass samples, the areas under the $K\alpha$ peaks of copper and zinc were obtained for each sample. The logarithm of the ratio of these two numbers was defined as log(Cu/Zn), measured. From the standard specification sheet, the logarithm of the percentage ratio of copper to zinc was found and defined as log(Cu/Zn), specification. Figure 1 illustrates a plot of log(Cu/Zn), specification *vs.* log(Cu/Zn), measured for several common brasses. In the case of the lead–tin solders, the areas under the $L\beta$ peak of lead and the $K\alpha$ peak of tin were obtained, and the logarithms of the measured and specification ratios of lead/tin were plotted and are also shown in Fig. 1. The $K\alpha$ peak of silver and the $L\beta$ peak of gold were used to obtain a similar plot for the gold–silver alloy.

Each set of points exhibits a definite trend which can be approximated by a smooth curve. The scatter about the line can perhaps be explained by different counting efficiencies for different X-ray

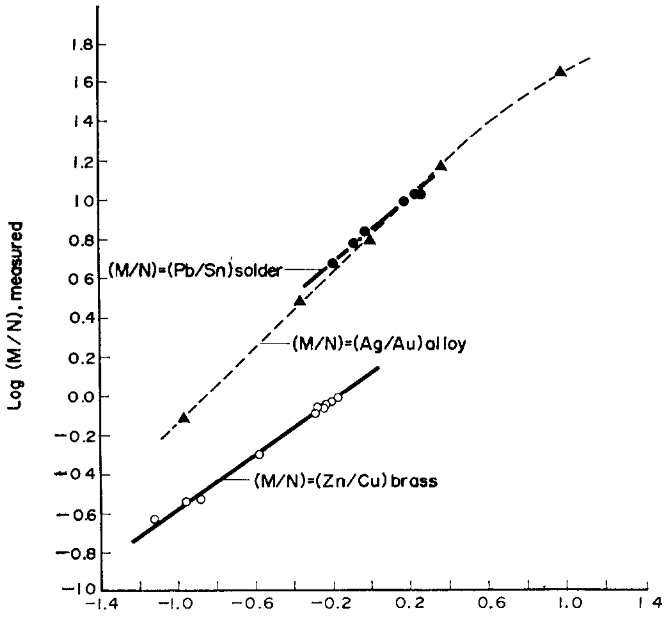


FIG. 1.—A plot of log(M/N), measured, *vs.* log(M/N), specification, for series of brass alloys, solders alloys and Ag–Au alloys illustrating that individual alloys can be identified by energy-dispersive X-ray spectroscopy.

fluxes, by differential absorption of X-rays in the sample as a function of X-ray energy, by fluorescence or absorption by trace elements, or by inhomogeneity in the sample. Since there is no requirement that the points fit a particular type of curve, this scatter does not invalidate the technique. The important fact is that each point represents a specific alloy and is a function only of the composition of the sample.

The reason for plotting ratios of elements is that this minimizes differences due to any physical discrepancies between one sample and another, *e.g.*, comparison of a small sample to a large sample, a smooth to a rough sample; also, it normalizes experimental irregularities such as differences in, counting times between samples.[4–5] This emphasises the fact that each point is a function, primarily of the composition of the sample and not of its physical features.

There are cases where two alloys may have almost identical major element composition and in the plot their points may be so close together that it is difficult to distinguish between them. Two examples of this are shown in the brass plot in the log(M/N), measured, region from −0·05 to −0·09 and in the log(M/N), specification, region from −0·2 to −0·3. However, in both cases one of the brasses is free-machining and has a lead content that is 20–30 times higher than that in the non-free-machining brass, represented by the adjoining point. The *L* series lines of lead in the case of the high lead-content alloys (free-machining) can easily be seen and thereby it is easy to distinguish between them and the adjoining low lead-content alloys. A somewhat similar occurrence is apparent at the top of the solder alloy points—two alloys are very close to one another. In this case, one of the alloys has 10 times the amounts of Cu, Sb, Ag and Bi that the other alloy has. Thus, characteristic X-ray lines of one or more of these elements are apparent for one alloy, but not for the other; therefore, the two alloys can be distinguished.

Although the applicability of this technique to a variety of alloy systems can be visualized, caution must be exercised in some cases. For example, a variation of the method can be used superficially for stainless steels. In ternary or more complex alloys, some measure must be made of all major elements to ensure that they are within specification. However, it would be preferred if the advantage could be retained of a data point representing the chemical composition of a sample, independent of physical characteristics such as size or surface finish. For ternary systems such as stainless steel (Fe, Cr, Ni), this can be accomplished by plotting ratios of two of the elements to the

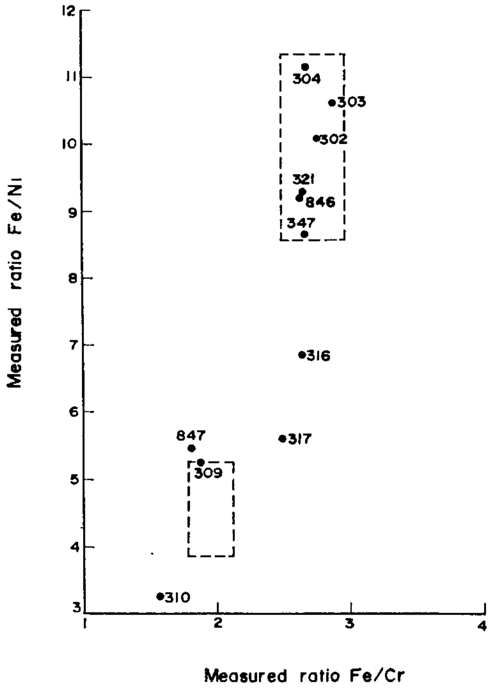


FIG. 2.—A plot of Fe/Ni *vs.* Fe/Cr ratios for stainless steels as determined by energy-dispersive X-ray spectroscopy illustrating that analysed steel alloys can be identified. The rectangles represent the variation in Cr and Ni contents that can be present in actual steel samples, Types 302 and 309 stainless steels, in this case.

third used as a normalizing factor. Figure 2 illustrates such a plot where the areas under the characteristic $K\alpha$ peaks for iron, chromium and nickel were obtained, the ratios Fe/Ni and Fe/Cr were determined and then plotted *vs.* each other. The point of this discussion is that, whereas analysed standards provide point plots, complex alloys such as stainless-steel samples yield area plots because the specifications for stainless steels do not specify a single percentage for iron, chromium or nickel. Rather, the specifications define ranges; *e.g.*, for an AISI Type 302 stainless steel, the chromium content must be between 17·00 and 19·00%, the nickel between 8·00 and 10·00%, there are maxima of 1·00% Si, 2·00% Mn and 0·15% C and the remainder is iron. Because of this, the Fe/Cr and Fe/Ni ratios can vary over an appreciable range—this range is designated for the Type 302 and 309 stainless steels by the rectangles in Fig. 2. Obviously, there is a great deal of overlapping than can occur among the various steels. Therefore, although it is possible to distinguish between a Type 304 steel and a Type 309, caution must be exercised in distinguishing between Types 304 and 347 (the presence of niobium would identify the Type 347). Other analytical techniques suffer from these overlapping compositions and experience difficulty in qualitatively characterizing a steel. Certainly, EDXS can distinguish between the various series of stainless steels since the chromium and nickel contents are quite different; this frequently is all the distinction necessary in production control.

The possible applications of this technique are numerous and include verification of composition on production lines, in stock control to ensure no mix-up in the inventory and in general laboratory work to identify the type of alloy in question. The last two uses have frequently been used in the authors' laboratory. Two of the outstanding advantages of this technique are the speed of identification and the ease with which the equipment can be operated.

Acknowledgements—The authors would like to express their appreciation to R. J. Baughman for preparing the Ag–Au alloy standards, to R. G. Dosch for the chemical analysis of the Ag–Au alloy standards and to D. E. Wanner and J. C. Russell for helpful discussions.

Spectroscopy Division
Sandia Laboratories
Albuquerque, New Mexico 87115, *U.S.A.*

P. E. HARRISON
B. T. KENNA

Summary—Energy dispersive X-ray spectroscopy can be used to identify alloy types quickly and, in many cases, to distinguish between alloy systems within a certain alloy type. Characteristic X-rays of major components in an alloy are produced through excitation by an isotopic source. Ratios of the X-ray intensities of a pair of elements are plotted *vs.* ratios of the theoretical weight fractions of these elements. This provides a unique data point which is a function of the composition of the particular alloy system. In some cases, characteristic X-rays of minor constituents are used for total identification.

Zusammenfassung—Die Röntgenspektroskopie mit Energiedispersion kann zur raschen Identifizierung von Legierungstypen und in vielen Fällen zur Unterscheidung zwischen Legierungssystemen innerhalb eines bestimmten Legierungstyps dienen. Die charakteristische Röntgenstrahlung der Hauptbestandteile einer Legierung wird mit Hilfe einer Isotopenquelle angeregt. Die Verhältnisse der Röntgenintensitäten eines Elementpaars werden gegen die Verhältnisse der theoretischen Gewichtsbrüche dieser Elemente aufgetragen. Das ergibt einen kennzeichnenden Satz von Daten, der von der Zusammensetzung des jeweiligen speziellen Legierungssystems abhängt. In einigen Fällen werden die charakteristischen Röntgenstrahlen von Nebenbestandteilen für die Identifizierung im Ganzen herangezogen.

Résumé—On peut utiliser la spectroscopie de rayons X à dispersion d'énergie pour identifier rapidement des types d'alliages et, dans de nombreux cas, pour distinguer les systèmes d'alliages à l'intérieur d'un certain type d'alliage. Des rayons X caractéristiques des composants majeurs d'un alliage sont produits par excitation par une source isotopique. On porte les rapports des intensités des rayons X d'une paire d'éléments en fonction des rapports des fractions de poids théoriques de ces éléments. Ceci fournit un point de données particulières qui est une fonction de la composition du système d'alliage concerné. Dans quelques cas, on utilise les rayons X caractéristiques de constituants mineurs pour l'identification totale.

REFERENCES

1. P. G. Burkhalter, *Anal. Chem.* 1971, **43**, 10.
2. J. W. Criss and L. S. Birks, *ibid.* 1968, **40**, 1080.
3. N. Stalnaker, M. Kahn and B. Kenna, *J. Radioanal. Chem.*, 1971 **7**, 81.
4. L. Bäckerud, *Appl. Spectry.*, 1967, **21**, 315.
5. J. Kinnunen, P. Rautavalta and M. Koponen, *Metallurgia*, 1967, **75**, 189.
6. E. Elad and M. Nakamura, *Nucl. Instr. Method*, 1966, **41**, 161.
7. J. P. Hurley, V. L. DaGragnanox and J. M. Mathiesen, *Research/Development*, 1970 (Dec.), 14.
8. R. D. Giauque, *Anal. Chem.*, 1968, **40**, 2075.
9. R. S. Frankel and D. W. Aitden, *Appl. Spectry.*, 1970, **24**, 557.
10. S. J. Zanin and G. E. Hooser, *ibid.*, 1968, **22**, 105.
11. J. R. Rhodes, ORO-3224-14, Final Report, *X-ray Analysis Using Radioisotope Sources*, Contract AT-(40-1)-3223, Texas Nuclear Corp., Austin, Texas, Sept. 25, 1968.
12. B. Sellers and J. Brinkerhoff, *Materials Research and Standards*, 1970 (Nov), 16.

Talanta, 1972, Vol. 19, pp. 814 to 817. Pergamon Press. Printed in Northern Ireland

6-phenyl-2,3-dihydro-*asym*-triazine-3-thione and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione as gravimetric reagents for the determination of thallium and palladium

(*Received* 27 *August* 1971. *Accepted* 18 *November* 1971)

SULPHUR-CONTAINING ligands show a marked selectivity for a relatively small number of transition metals. In this work the analytical applications of two sulphur-containing ligands, 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) were investigated.

Procedure

Weigh a sample of a size based on the expected homogeneity of the alloy, place it in a 250-ml beaker, dissolve it in *aqua regia*, then remove the cover glass and evaporate to dryness under infrared drying lamps. Cool, add 20 ml of conc. hydrochloric acid, rinse down the sides of the beaker and again evaporate to dryness under the lamps. Repeat this operation at least twice more for the complete removal of nitrate. Cool, add 20–30 ml of $9M$ hydrochloric acid to dissolve the metal salts, transfer the sample solution to a suitable volumetric flask, dilute to volume with $9M$ hydrochloric acid and mix thoroughly. Transfer a suitable aliquot containing not more than 20 μg of zirconium or 50 μg of hafnium to a 50 ml volumetric flask containing 25 ml of $9M$ hydrochloric acid. Prepare a similar reagent blank. Add 4 ml of Arsenazo III solution to each flask, dilute to volume with $9M$ hydrochloric acid, mix, measure the absorbance for samples and the blank. Apply the blank correction.

RESULTS

The procedure was applied to four molybdenum alloys, with the results shown in Tables I and II. The results show good agreement with accepted values, and are reproducible. The method is simple and no prior separation is necessary. The relative standard deviation ranges from 1·3 to 2·7%.

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135, *U.S.A.*

WILLIAM A. DUPRAW

Summary—A simple analytical procedure is described for determining zirconium or hafnium in molybdenum-base alloys by formation of the Arsenazo III complex of zirconium or hafnium in $9M$ hydrochloric acid medium. The absorbance is measured at 670 nm. Molybdenum (10 mg), titanium (1 mg), and rhenium (10 mg) have no adverse effect. No prior separation is needed. The relative standard deviation is 1·3–2·7%.

Zusammenfassung—Ein einfaches analytisches Verfahren zur Bestimmung von Zirkonium oder Hafnium in Legierungen auf Molybdängrundlage wird beschrieben. Es beruht auf der Bildung des Komplexes von Zirkonium oder Hafnium mit Arsenazo III in 9 M Salzsäure. Die Extinktion wird bei 670 nm gemessen. 10 mg Molybdän, 1 mg Titan und 10 mg Rhenium stören nicht. Es ist keine vorhergehende Abtrennung notwendig. Die relative Standardabweichung betragt 1,3–2,7%.

Résumé—On décrit une technique analytique simple pour le dosage du zirconium ou du hafnium dans les alliages à base de molybdène par formation du complexe Arsenazo III du zirconium ou du hafnium en milieu acide chlorhydrique $9M$. On mesure l'absorption à 670 nm. Le molybdène (10 mg), le titane (1 mg) et le rhénium (10 mg) n'ont pas d'effet défavorable. Une séparation préalable n'est pas nécessaire. L'écart type relatif est 1,3–2,7%.

REFERENCES

1. S. B. Savvin, *Talanta*, 1964, **11**, 7.
2. O. A. Vita, *Goodyear Atomic Corporation Report* GAT-524, 1966.
3. D. L. Chase, *Battelle Memorial Institute DMIC Report* 220, 1965.

Talanta, 1972, Vol. 19, pp. 810 to 814. Pergamon Press. Printed in Northern Ireland

Qualitative identification of alloys by energy-dispersive X-ray spectroscopy*

(*Received* 23 *September* 1971. *Accepted* 14 *November* 1971)

ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDXS) has been advancing rapidly in recent years, largely on account of the development of high-resolution semiconductor detectors and the increasing availability of radioisotopic sources suitable for use in excitation. The use of this technique for quantitative

* This work was supported by the United States Atomic Energy Commission.

analysis involves inherent difficulties, one of the main problems being differences in matrix effects when samples and standards are not identical in chemical and physical characteristics. However, there are means whereby these problems may be minimized.[1–5] The literature contains numerous papers[6–12] on the technique, the application to quantitative analyses, and descriptions of radioisotope source assemblies. Therefore, the theory of the method and the varied applications will not be presented here.

The application of EDXS to qualitative analysis is relatively rapid and generally straightforward. The $K\alpha$ and $K\beta$ or $L\alpha$, $L\beta$, and $L\gamma$ peaks obtained experimentally can be compared with the corresponding peaks obtained from standards or with tabulated values, to obtain qualitative identification. By use of a source which emits photons with a definite maximum energy, either in the form of X-rays, gamma-rays or bremsstrahlung, the range of elements which can be excited and caused to emit characteristic X-rays can be controlled. There are a number of commercially available radioisotopic sources and required sources that are not available can be prepared. The sensitivity, which is dependent on a number of parameters such as matrix, atomic number and excitation source, is in the range from parts per thousand to parts per million for most elements. For $18 > Z > 10$, the use of helium or vacuum, rather than air, in the apparatus is necessary. Elements with $Z < 10$ are not directly detectable by this technique.

In an analytical laboratory, the use of EDXS for qualitative analysis can relieve the sample load on other methods such as emission spectroscopy. Since these other techniques are capable of identifying specific alloys, full utilization of EDXS should include qualitative identification of alloys.

Although Sellers and Brinkerhoff[12] have suggested a technique for alloy sorting which uses energy filters and multiple counts, the method described in this paper requires only one sample counting and no filters are needed. The experimental results are incorporated with specification data in a graph which permits unique identification of a specific alloy within an alloy type.

EXPERIMENTAL

Instrumentation

A Nuclear Diodes EDXS system, Model XS-25-240-DSS, was used in this work. The Si(Li) detector was 25 mm^2 × 3 mm and had a 2-mil beryllium window. The signals were passed through an amplifier into a TMC 404C analyser. The system resolution was <300 eV FWHM (full peak width at half the maximum peak height) for the 6·4 keV $K\alpha$ X-rays of iron.

Samples were supported on a Mylar film stretched across a Nuclear Diodes Model XFS-1 source-holder. The sources were mounted in the holder such that line of sight between the source and sample was at 45° to the axis defined by the sample and detector. The holder shielded the detector from direct bombardment by the source and also served to collimate the X-rays generated in the sample.

Excitation

Samples were placed by hand in the centre of the Mylar film as reproducibly as possible. ^{241}Am and ^{109}Cd sources were used individually for excitation of the characteristic X-ray lines of the samples. Accumulation of the spectra was for either 1 or 4 min, depending on the size of the samples and the intensity of the X-rays produced. The areas under the individual peaks of interest were obtained by integration with a TMC Resolver/Integrator unit.

Samples

The samples used in this work were NBS SRM brass standards (standards C1103–C1119), lead–tin solder spectrochemical standards obtained from Morris P. Kirk Co. (standard numbers 527–585), analysed stainless steel (austenitic) from Armco Steel Co., Rustless Division and a gold–silver alloy series prepared in this laboratory and analysed by standard wet chemical procedures.

RESULTS AND DISCUSSION

In the case of the brass samples, the areas under the $K\alpha$ peaks of copper and zinc were obtained for each sample. The logarithm of the ratio of these two numbers was defined as log(Cu/Zn), measured. From the standard specification sheet, the logarithm of the percentage ratio of copper to zinc was found and defined as log(Cu/Zn), specification. Figure 1 illustrates a plot of log(Cu/Zn), specification *vs.* log(Cu/Zn), measured for several common brasses. In the case of the lead–tin solders, the areas under the $L\beta$ peak of lead and the $K\alpha$ peak of tin were obtained, and the logarithms of the measured and specification ratios of lead/tin were plotted and are also shown in Fig. 1. The $K\alpha$ peak of silver and the $L\beta$ peak of gold were used to obtain a similar plot for the gold–silver alloy.

Each set of points exhibits a definite trend which can be approximated by a smooth curve. The scatter about the line can perhaps be explained by different counting efficiencies for different X-ray

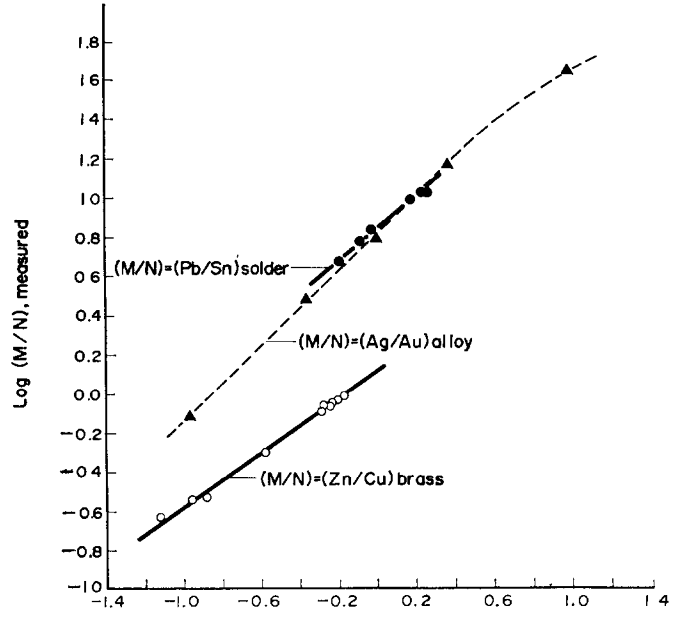


FIG. 1.—A plot of log(M/N), measured, *vs.* log(M/N), specification, for series of brass alloys, solders alloys and Ag–Au alloys illustrating that individual alloys can be identified by energy-dispersive X-ray spectroscopy.

fluxes, by differential absorption of X-rays in the sample as a function of X-ray energy, by fluorescence or absorption by trace elements, or by inhomogeneity in the sample. Since there is no requirement that the points fit a particular type of curve, this scatter does not invalidate the technique. The important fact is that each point represents a specific alloy and is a function only of the composition of the sample.

The reason for plotting ratios of elements is that this minimizes differences due to any physical discrepancies between one sample and another, *e.g.*, comparison of a small sample to a large sample, a smooth to a rough sample; also, it normalizes experimental irregularities such as differences in, counting times between samples.[4–6] This emphasises the fact that each point is a function, primarily of the composition of the sample and not of its physical features.

There are cases where two alloys may have almost identical major element composition and in the plot their points may be so close together that it is difficult to distinguish between them. Two examples of this are shown in the brass plot in the log(M/N), measured, region from —0·05 to —0·09 and in the log(M/N), specification, region from —0·2 to —0·3. However, in both cases one of the brasses is free-machining and has a lead content that is 20–30 times higher than that in the non-free-machining brass, represented by the adjoining point. The *L* series lines of lead in the case of the high lead-content alloys (free-machining) can easily be seen and thereby it is easy to distinguish between them and the adjoining low lead-content alloys. A somewhat similar occurrence is apparent at the top of the solder alloy points—two alloys are very close to one another. In this case, one of the alloys has 10 times the amounts of Cu, Sb, Ag and Bi that the other alloy has. Thus, characteristic X-ray lines of one or more of these elements are apparent for one alloy, but not for the other; therefore, the two alloys can be distinguished.

Although the applicability of this technique to a variety of alloy systems can be visualized, caution must be exercised in some cases. For example, a variation of the method can be used superficially for stainless steels. In ternary or more complex alloys, some measure must be made of all major elements to ensure that they are within specification. However, it would be preferred if the advantage could be retained of a data point representing the chemical composition of a sample, independent of physical characteristics such as size or surface finish. For ternary systems such as stainless steel (Fe, Cr, Ni), this can be accomplished by plotting ratios of two of the elements to the

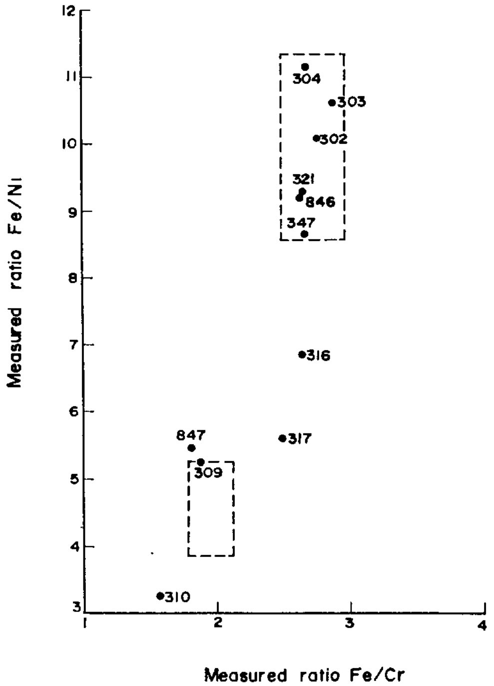


FIG. 2.—A plot of Fe/Ni *vs.* Fe/Cr ratios for stainless steels as determined by energy-dispersive X-ray spectroscopy illustrating that analysed steel alloys can be identified. The rectangles represent the variation in Cr and Ni contents that can be present in actual steel samples, Types 302 and 309 stainless steels, in this case.

third used as a normalizing factor. Figure 2 illustrates such a plot where the areas under the characteristic $K\alpha$ peaks for iron, chromium and nickel were obtained, the ratios Fe/Ni and Fe/Cr were determined and then plotted *vs.* each other. The point of this discussion is that, whereas analysed standards provide point plots, complex alloys such as stainless-steel samples yield area plots because the specifications for stainless steels do not specify a single percentage for iron, chromium or nickel. Rather, the specifications define ranges; *e.g.*, for an AISI Type 302 stainless steel, the chromium content must be between 17·00 and 19·00%, the nickel between 8·00 and 10·00%, there are maxima of 1·00% Si, 2·00% Mn and 0·15% C and the remainder is iron. Because of this, the Fe/Cr and Fe/Ni ratios can vary over an appreciable range—this range is designated for the Type 302 and 309 stainless steels by the rectangles in Fig. 2. Obviously, there is a great deal of overlapping than can occur among the various steels. Therefore, although it is possible to distinguish between a Type 304 steel and a Type 309, caution must be exercised in distinguishing between Types 304 and 347 (the presence of niobium would identify the Type 347). Other analytical techniques suffer from these overlapping compositions and experience difficulty in qualitatively characterizing a steel. Certainly, EDXS can distinguish between the various series of stainless steels since the chromium and nickel contents are quite different; this frequently is all the distinction necessary in production control.

The possible applications of this technique are numerous and include verification of composition on production lines, in stock control to ensure no mix-up in the inventory and in general laboratory work to identify the type of alloy in question. The last two uses have frequently been used in the authors' laboratory. Two of the outstanding advantages of this technique are the speed of identification and the ease with which the equipment can be operated.

Acknowledgements—The authors would like to express their appreciation to R. J. Baughman for preparing the Ag–Au alloy standards, to R. G. Dosch for the chemical analysis of the Ag–Au alloy standards and to D. E. Wanner and J. C. Russell for helpful discussions.

Spectroscopy Division
Sandia Laboratories
Albuquerque, New Mexico 87115, *U.S.A.*

P. E. HARRISON
B. T. KENNA

Summary—Energy dispersive X-ray spectroscopy can be used to identify alloy types quickly and, in many cases, to distinguish between alloy systems within a certain alloy type. Characteristic X-rays of major components in an alloy are produced through excitation by an isotopic source. Ratios of the X-ray intensities of a pair of elements are plotted *vs.* ratios of the theoretical weight fractions of these elements. This provides a unique data point which is a function of the composition of the particular alloy system. In some cases, characteristic X-rays of minor constituents are used for total identification.

Zusammenfassung—Die Röntgenspektroskopie mit Energiedispersion kann zur raschen Identifizierung von Legierungstypen und in vielen Fällen zur Unterscheidung zwischen Legierungssystemen innerhalb eines bestimmten Legierungstyps dienen. Die charakteristische Röntgenstrahlung der Hauptbestandteile einer Legierung wird mit Hilfe einer Isotopenquelle angeregt. Die Verhältnisse der Röntgenintensitäten eines Elementpaars werden gegen die Verhältnisse der theoretischen Gewichtsbrüche dieser Elemente aufgetragen. Das ergibt einen kennzeichnenden Satz von Daten, der von der Zusammensetzung des jeweiligen speziellen Legierungssystems abhängt. In einigen Fällen werden die charakteristischen Röntgenstrahlen von Nebenbestandteilen für die Identifizierung im Ganzen herangezogen.

Résumé—On peut utiliser la spectroscopie de rayons X à dispersion d'énergie pour identifier rapidement des types d'alliages et, dans de nombreux cas, pour distinguer les systèmes d'alliages à l'intérieur d'un certain type d'alliage. Des rayons X caractéristiques des composants majeurs d'un alliage sont produits par excitation par une source isotopique. On porte les rapports des intensités des rayons X d'une paire d'éléments en fonction des rapports des fractions de poids théoriques de ces éléments. Ceci fournit un point de données particulières qui est une fonction de la composition du système d'alliage concerné. Dans quelques cas, on utilise les rayons X caractéristiques de constituants mineurs pour l'identification totale.

REFERENCES

1. P. G. Burkhalter, *Anal. Chem.* 1971, **43**, 10.
2. J. W. Criss and L. S. Birks, *ibid.* 1968, **40**, 1080.
3. N. Stalnaker, M. Kahn and B. Kenna, *J. Radioanal. Chem.*, 1971 **7**, 81.
4. L. Bäckerud, *Appl. Spectry.*, 1967, **21**, 315.
5. J. Kinnunen, P. Rautavalta and M. Koponen, *Metallurgia*, 1967, **75**, 189.
6. E. Elad and M. Nakamura, *Nucl. Instr. Method*, 1966, **41**, 161.
7. J. P. Hurley, V. L. DaGragnanox and J. M. Mathiesen, *Research/Development*, 1970 (Dec.), 14.
8. R. D. Giauque, *Anal. Chem.*, 1968, **40**, 2075.
9. R. S. Frankel and D. W. Aitden, *Appl. Spectry.*, 1970, **24**, 557.
10. S. J. Zanin and G. E. Hooser, *ibid.*, 1968, **22**, 105.
11. J. R. Rhodes, ORO-3224-14, Final Report, *X-ray Analysis Using Radioisotope Sources*, Contract AT-(40-1)-3223, Texas Nuclear Corp., Austin, Texas, Sept. 25, 1968.
12. B. Sellers and J. Brinkerhoff, *Materials Research and Standards*, 1970 (Nov), 16.

Talanta, 1972, Vol. 19, pp. 814 to 817. Pergamon Press. Printed in Northern Ireland

6-phenyl-2,3-dihydro-*asym*-triazine-3-thione and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione as gravimetric reagents for the determination of thallium and palladium

(*Received* 27 *August* 1971. *Accepted* 18 *November* 1971)

SULPHUR-CONTAINING ligands show a marked selectivity for a relatively small number of transition metals. In this work the analytical applications of two sulphur-containing ligands, 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) were investigated.

Summary—Energy dispersive X-ray spectroscopy can be used to identify alloy types quickly and, in many cases, to distinguish between alloy systems within a certain alloy type. Characteristic X-rays of major components in an alloy are produced through excitation by an isotopic source. Ratios of the X-ray intensities of a pair of elements are plotted *vs.* ratios of the theoretical weight fractions of these elements. This provides a unique data point which is a function of the composition of the particular alloy system. In some cases, characteristic X-rays of minor constituents are used for total identification.

Zusammenfassung—Die Röntgenspektroskopie mit Energiedispersion kann zur raschen Identifizierung von Legierungstypen und in vielen Fällen zur Unterscheidung zwischen Legierungssystemen innerhalb eines bestimmten Legierungstyps dienen. Die charakteristische Röntgenstrahlung der Hauptbestandteile einer Legierung wird mit Hilfe einer Isotopenquelle angeregt. Die Verhältnisse der Röntgenintensitäten eines Elementpaars werden gegen die Verhältnisse der theoretischen Gewichtsbrüche dieser Elemente aufgetragen. Das ergibt einen kennzeichnenden Satz von Daten, der von der Zusammensetzung des jeweiligen speziellen Legierungssystems abhängt. In einigen Fällen werden die charakteristischen Röntgenstrahlen von Nebenbestandteilen für die Identifizierung im Ganzen herangezogen.

Résumé—On peut utiliser la spectroscopie de rayons X à dispersion d'énergie pour identifier rapidement des types d'alliages et, dans de nombreux cas, pour distinguer les systèmes d'alliages à l'intérieur d'un certain type d'alliage. Des rayons X caractéristiques des composants majeurs d'un alliage sont produits par excitation par une source isotopique. On porte les rapports des intensités des rayons X d'une paire d'éléments en fonction des rapports des fractions de poids théoriques de ces éléments. Ceci fournit un point de données particulières qui est une fonction de la composition du système d'alliage concerné. Dans quelques cas, on utilise les rayons X caractéristiques de constituants mineurs pour l'identification totale.

REFERENCES

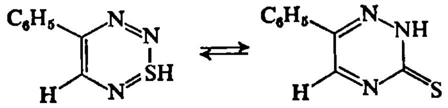
1. P. G. Burkhalter, *Anal. Chem.* 1971, **43**, 10.
2. J. W. Criss and L. S. Birks, *ibid.* 1968, **40**, 1080.
3. N. Stalnaker, M. Kahn and B. Kenna, *J. Radioanal. Chem.*, 1971 **7**, 81.
4. L. Bäckerud, *Appl. Spectry.*, 1967, **21**, 315.
5. J. Kinnunen, P. Rautavalta and M. Koponen, *Metallurgia*, 1967, **75**, 189.
6. E. Elad and M. Nakamura, *Nucl. Instr. Method*, 1966, **41**, 161.
7. J. P. Hurley, V. L. DaGragnanox and J. M. Mathiesen, *Research/Development*, 1970 (Dec.), 14.
8. R. D. Giauque, *Anal. Chem.*, 1968, **40**, 2075.
9. R. S. Frankel and D. W. Aitden, *Appl. Spectry.*, 1970, **24**, 557.
10. S. J. Zanin and G. E. Hooser, *ibid.*, 1968, **22**, 105.
11. J. R. Rhodes, ORO-3224-14, Final Report, *X-ray Analysis Using Radioisotope Sources*, Contract AT-(40-1)-3223, Texas Nuclear Corp., Austin, Texas, Sept. 25, 1968.
12. B. Sellers and J. Brinkerhoff, *Materials Research and Standards*, 1970 (Nov), 16.

Talanta, 1972, Vol. 19, pp. 814 to 817. Pergamon Press. Printed in Northern Ireland

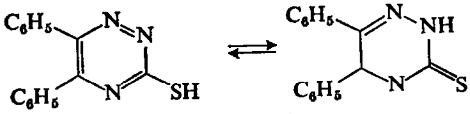
6-phenyl-2,3-dihydro-*asym*-triazine-3-thione and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione as gravimetric reagents for the determination of thallium and palladium

(*Received* 27 *August* 1971. *Accepted* 18 *November* 1971)

SULPHUR-CONTAINING ligands show a marked selectivity for a relatively small number of transition metals. In this work the analytical applications of two sulphur-containing ligands, 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) were investigated.



(PDTT)



(DDTT)

They are both yellow powders insoluble in water, soluble in ethanol, chloroform and aqueous alkaline solutions.

Preliminary investigations showed that of the 35 metal ions examined in tartrate media of pH 8·5–12·5 only Pd(II), Cu(II), Hg(II), Ag(I) and Tl(I) could be precipitated by PDTT and that on the addition of cyanide only thallium(I) gave a precipitate. The DDTT reagent is more selective as it only gives precipitates with Hg(II), Ag(I), Pd(II) and Tl(I), but no reaction with copper. It proved useful for the determination of palladium. All the precipitates are yellow except the Cu–PDTT complex which is orange-red.

EXPERIMENTAL

Reagents

PDTT. Prepared by the procedure of Lalezari and Golgolab[1] by one-step cyclization of phenylglyoxaldoxime and thiosemicarbazide in dilute hydrochloric acid and recrystallized from dimethylsulphoxide to give dark yellow crystals: m.p. 242–243°, yield 90%.

DDTT. Prepared by the method of Polonovski and Pesson[2] by interaction of benzil and thiosemicarbazide in boiling acetic acid and recrystallized from ethanol to give yellow crystals: m.p. 217–218°, yield 60%.

Reagent solutions (0·5%) are prepared by dissolving the reagents in 1*M* sodium hydroxide and filtering.

Standard solutions of thallium and palladium. Dissolve the pure metals in nitric acid and hydrochloric acid respectively.

Procedure

A solution containing 5–50 mg of palladium(II) or thallium(I) per 100 ml is prepared and to this 10 ml of 10% ammonium tartrate solution are added. The pH of this solution is adjusted to 10–12 with dilute sodium hydroxide solution and 1*M* tartaric acid. The solution is warmed and a 20% excess of the reagent is added with stirring. The precipitate is digested for 10 min on the water-bath and then filtered off on a sintered-glass crucible (porosity 4) and washed with about 100 ml of hot water. The precipitate is dried at 110° for 30 min. For the determination of palladium, DDTT reagent is used and the precipitate is weighed as $Pd(C_{15}H_{10}N_3S)_2$ which contains 16·75% of palladium. For the determination of thallium, PDTT reagent is used and the precipitate is weighed as $TlC_9H_6N_3S$ which contains 52·00% of thallium.

RESULTS AND DISCUSSION

Solutions of the reagents in sodium hydroxide are stable indefinitely. The solid sodium salts of the reagents, recovered from aqueous sodium hydroxide solutions, were orange powders stable up to 360° and moderately soluble in chloroform. Analysis of the precipitates of the palladium and thallium complexes prepared according to the recommended gravimetric procedures are given in Table I and results of gravimetric determination of palladium(II) and thallium(I) are given in Table II.

TABLE I.—ANALYTICAL DATA OF PALLADIUM AND THALLIUM COMPLEXES

	C, %	H, %	N, %	S, %	Decomposition temperature, °*C*
$Pd(C_{15}H_{10}N_3S)_2$					
required	56·75	3·15	13·24	10·12	
found	56·7	3·2	13·3	10·0	248–250
$Tl\ C_9H_6N_3S$					
required	27·35	1·58	10·65	8·25	
found	27·3	1·6	10·6	8·2	150–152

TABLE II.—RESULTS OF DETERMINATION OF PALLADIUM AND THALLIUM

Pd taken, *mg*	Pd found, *mg*	Relative error %	Tl taken, *mg*	Tl found, *mg*	Relative error %
5·0	5·1	2	6·2	6·1	−2
11·3	11·2	−1	12·5	12·5	0
25·4	25·5	+0·4	25·0	25·1	+0·4
33·9	34·0	+0·3	37·5	37·4	−0·3

When cyanide was used as a masking agent DDTT still gave a yellow precipitate with thallium(I) in alkaline solution. The precipitation is specific but unsuitable for gravimetry because the precipitate has a low decomposition temperature (110–112°).

The precipitation of thallium(I) by PDTT and palladium(II) by DDTT is quantitative over the pH range 9–13. Both precipitates are yellow, crystalline, and non-hygroscopic and can easily be dried at 110°. The thermograms of the two metal complexes have been recorded (Fig. 1). Tl–PDTT (curve *a*) decomposes at temperatures above 150° and Pd–DDTT (curve *b*) is stable up to at least 240°. Pd(II)–DDTT complex is soluble in chloroform ($\varepsilon = 2{\cdot}3 \times 10^4$ l. mole^{-1}.cm^{-1} at 250 nm). An attempt to extract this complex into chloroform and measure it spectrophotometrically failed because the excess of reagent ($\lambda_{max} = 315$ nm in chloroform) is also extracted and causes non-reproducible results.

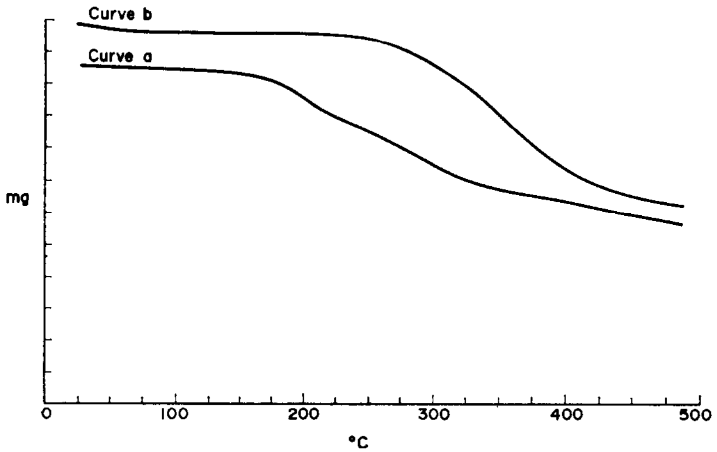


FIG. 1.—Thermograms of (*a*) Tl–PDTT; (*b*) Pd(II)–DDTT.

In the precipitation of palladium a 100-fold excess of Au(III), Bi, Cu(II), Fe(III), Pb, Co(II) and Ni give an error within ±2%. Sn(II) must be oxidized to Sn(IV) by addition of appropriate amounts of iron(III) chloride to prevent its hydrolysis in alkaline tartrate medium. Hg(II), Ag and Tl(I) will interfere in the gravimetric determination of palladium(II). The method is more sensitive than the dimethylglyoxime method. The precipitation of thallium as the PDTT complex is specific but less sensitive than the thionalide method.[3,4] In the presence of cyanide a 100-fold excess of Pd(II), Cu(II) or Ag did not cause significant error in the determination of thallium.

Department of Chemistry and Chemical Engineering M. EDRISSI
Teheran Polytechnique, Iran

Department of Chemistry, Pahlavi University A. MASSOUMI
Shiraz, Iran

Department of Chemistry, Faculty of Pharmacy I. LALEZARI
University of Teheran, Teheran, Iran

Summary—The analytical use of 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) has been investigated. PDTT proved to be suitable for the

determination of thallium(I) in the presence of cyanide whereas DDTT is more selective than PDTT in alkaline tartrate solution and is applied for the selective gravimetric determination of palladium. The method is more sensitive than the dimethylglyoxime method. The only metal ions interfering are Hg(II), Ag and Tl(I).

Zusammenfassung—Die analytische Verwendbarkeit von 6-Phenyl-2,3-dihydro-*asym*-triazin-3-thion (PDTT) und 5,6-Diphenyl-2,3-dihydro-*asym*-triazin-3-thion (DDTT) wurde untersucht. PDTT ist zur Bestimmung von Thallium(I) in Gegenwart von Cyanid geeignet, DDTT ist in alkalischer Tartratlösung selektiver als PDTT und wird zur selektiven gravimetrischen Bestimmung von Palladium verwendet. Das Verfahren ist empfindlicher als das mit Dimethylglyoxim. An Metallionen stören nur Hg(II), Ag und Tl(I).

Résumé—On a étudié l'usage analytique de la 6-phényl 2,3-dihydro-*asym*-triazine 3-thione (PDTT) et de la 5,6-diphényl 2,3-dihydro-*asym*-triazine 3-thione (DDTT). La PDTT s'est avérée convenable pour le dosage du thallium(I) en la présence de cyanure, tandis que la DDTT est plus sélective que la PDTT en solution de tartrate alcalin et est appliquée au dosage gravimétrique sélectif du palladium. La méthode est plus sensible que la méthode à la diméthylglyoxime. Les seuls ions métalliques gênants sont Hg(II), Ag et Tl(I).

REFERENCES

1. I. Lalezari and H. Golgolab, *J. Heterocyclic Chem.*, 1970, **7**, 689.
2. M. Polonovski and M. Pesson, *Compt. Rend*, 1951, **232**, 1260.
3. I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part II, Volume 2, p. 60. Interscience, New York, 1962.
4. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., p. 549. Longmans, London, 1962.

Talanta, 1972, Vol. 19, pp. 817 to 821. Pergamon Press. Printed in Northern Ireland

Darstellung einer neuen Organoselenverbindung $(C_6H_5COCH_2)_4Se$, und ihre Anwendung zur Extraction von Selen. Bestimmung von Tellurspuren in reinem Selen

(*Eingegangen am* 5. *Juli* 1971. *Angenommen am* 2. *Dezember* 1971)

Es WERDEN organische Verbindungen des Selens mit gesättigten Monoketonen dargestellt—$(RCOCHR')_2SeCl_2$ (R und R′ sind Alkyl- und Arylradikale)[1–8] die sich weder in Chloroform noch in Tetrachlorkohlenstoff oder Benzol leicht lösen, bedingt durch ihre polaren Charakter da sie leicht löslich sind in polaren Lösungsmitteln. Unser Ziel ist es, um die analytische Anwendung selenorganischen Verbindungen zu erweitern, polare Verbindungen darzustellen, die in Chloroform oder Tetrachlorkohlenstoff gut löslich sind, und die Extraktionsabtrennungen von großen Mengen Selens gewährleisten. Wir wählten also die vollständig organosubstituierte Verbindung des Typs $(RCOCHR')_4Se$ und verwendet Acetophenon als Ligand, da $(C_6H_5COCH_2)_2SeCl_2$ in festem Zustand mühelos erhalten wird und von uns besser erforscht ist.[7]

DARSTELLUNG UND EIGENSCHAFTEN VON $(C_6H_5COCH_2)_4Se$

Es werden 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3) in 20–25 ml 8,5*M* Salzsäure aufgelöst und 3 ml Acetophenon zugesetzt, entsprechend dem molaren Verhältnis Selen:Acetophenon = 1:4. Nach 1,5–2 Std. tritt das Selen in Verbindung quantitativ auf, als weißer Niederschlag der Zusammensetzung $(C_6H_5COCH_2)_2SeCl_2$.[6,7] Nach 350–400 stündigem Stehen wandelt sich der Niederschlag in ein gelb-grünes ölartiges Produkt um. Bei einem größeren Überschuß an Acetophenon steigt die Reaktionsgeschwindigkeit. Da unsere Versuche, mußte die Zusammensetzung des Produktes indirekt bestimmt werden. Als Kennzeichnungsmerkmal des Systems Selen–Acetophenon–Salzsäure wählten wir die Extrahierbarkeit der entstehenden Produkte durch Chloroform. Die Verteilung des Selens in den beiden Phasen ist in Abb. 1 angegeben.

Summary—Energy dispersive X-ray spectroscopy can be used to identify alloy types quickly and, in many cases, to distinguish between alloy systems within a certain alloy type. Characteristic X-rays of major components in an alloy are produced through excitation by an isotopic source. Ratios of the X-ray intensities of a pair of elements are plotted *vs.* ratios of the theoretical weight fractions of these elements. This provides a unique data point which is a function of the composition of the particular alloy system. In some cases, characteristic X-rays of minor constituents are used for total identification.

Zusammenfassung—Die Röntgenspektroskopie mit Energiedispersion kann zur raschen Identifizierung von Legierungstypen und in vielen Fällen zur Unterscheidung zwischen Legierungssystemen innerhalb eines bestimmten Legierungstyps dienen. Die charakteristische Röntgenstrahlung der Hauptbestandteile einer Legierung wird mit Hilfe einer Isotopenquelle angeregt. Die Verhältnisse der Röntgenintensitäten eines Elementpaars werden gegen die Verhältnisse der theoretischen Gewichtsbrüche dieser Elemente aufgetragen. Das ergibt einen kennzeichnenden Satz von Daten, der von der Zusammensetzung des jeweiligen speziellen Legierungssystems abhängt. In einigen Fällen werden die charakteristischen Röntgenstrahlen von Nebenbestandteilen für die Identifizierung im Ganzen herangezogen.

Résumé—On peut utiliser la spectroscopie de rayons X à dispersion d'énergie pour identifier rapidement des types d'alliages et, dans de nombreux cas, pour distinguer les systèmes d'alliages à l'intérieur d'un certain type d'alliage. Des rayons X caractéristiques des composants majeurs d'un alliage sont produits par excitation par une source isotopique. On porte les rapports des intensités des rayons X d'une paire d'éléments en fonction des rapports des fractions de poids théoriques de ces éléments. Ceci fournit un point de données particulières qui est une fonction de la composition du système d'alliage concerné. Dans quelques cas, on utilise les rayons X caractéristiques de constituants mineurs pour l'identification totale.

REFERENCES

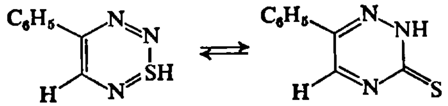
1. P. G. Burkhalter, *Anal. Chem.* 1971, **43**, 10.
2. J. W. Criss and L. S. Birks, *ibid.* 1968, **40**, 1080.
3. N. Stalnaker, M. Kahn and B. Kenna, *J. Radioanal. Chem.*, 1971 **7**, 81.
4. L. Bäckerud, *Appl. Spectry.*, 1967, **21**, 315.
5. J. Kinnunen, P. Rautavalta and M. Koponen, *Metallurgia*, 1967, **75**, 189.
6. E. Elad and M. Nakamura, *Nucl. Instr. Method*, 1966, **41**, 161.
7. J. P. Hurley, V. L. DaGragnanox and J. M. Mathiesen, *Research/Development*, 1970 (Dec.), 14.
8. R. D. Giauque, *Anal. Chem.*, 1968, **40**, 2075.
9. R. S. Frankel and D. W. Aitden, *Appl. Spectry.*, 1970, **24**, 557.
10. S. J. Zanin and G. E. Hooser, *ibid.*, 1968, **22**, 105.
11. J. R. Rhodes, ORO-3224-14, Final Report, *X-ray Analysis Using Radioisotope Sources*, Contract AT-(40-1)-3223, Texas Nuclear Corp., Austin, Texas, Sept. 25, 1968.
12. B. Sellers and J. Brinkerhoff, *Materials Research and Standards*, 1970 (Nov), 16.

Talanta, 1972, Vol. 19, pp. 814 to 817. Pergamon Press. Printed in Northern Ireland

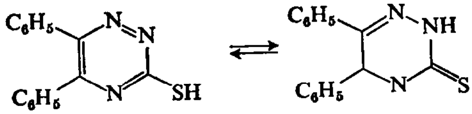
6-phenyl-2,3-dihydro-*asym*-triazine-3-thione and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione as gravimetric reagents for the determination of thallium and palladium

(*Received* 27 *August* 1971. *Accepted* 18 *November* 1971)

SULPHUR-CONTAINING ligands show a marked selectivity for a relatively small number of transition metals. In this work the analytical applications of two sulphur-containing ligands, 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) were investigated.



(PDTT)



(DDTT)

They are both yellow powders insoluble in water, soluble in ethanol, chloroform and aqueous alkaline solutions.

Preliminary investigations showed that of the 35 metal ions examined in tartrate media of pH 8·5–12·5 only Pd(II), Cu(II), Hg(II), Ag(I) and Tl(I) could be precipitated by PDTT and that on the addition of cyanide only thallium(I) gave a precipitate. The DDTT reagent is more selective as it only gives precipitates with Hg(II), Ag(I), Pd(II) and Tl(I), but no reaction with copper. It proved useful for the determination of palladium. All the precipitates are yellow except the Cu–PDTT complex which is orange-red.

EXPERIMENTAL

Reagents

PDTT. Prepared by the procedure of Lalezari and Golgolab[1] by one-step cyclization of phenylglyoxaldoxime and thiosemicarbazide in dilute hydrochloric acid and recrystallized from dimethylsulphoxide to give dark yellow crystals: m.p. 242–243°, yield 90%.

DDTT. Prepared by the method of Polonovski and Pesson[2] by interaction of benzil and thiosemicarbazide in boiling acetic acid and recrystallized from ethanol to give yellow crystals: m.p. 217–218°, yield 60%.

Reagent solutions (0·5%) are prepared by dissolving the reagents in 1*M* sodium hydroxide and filtering.

Standard solutions of thallium and palladium. Dissolve the pure metals in nitric acid and hydrochloric acid respectively.

Procedure

A solution containing 5–50 mg of palladium(II) or thallium(I) per 100 ml is prepared and to this 10 ml of 10% ammonium tartrate solution are added. The pH of this solution is adjusted to 10–12 with dilute sodium hydroxide solution and 1*M* tartaric acid. The solution is warmed and a 20% excess of the reagent is added with stirring. The precipitate is digested for 10 min on the water-bath and then filtered off on a sintered-glass crucible (porosity 4) and washed with about 100 ml of hot water. The precipitate is dried at 110° for 30 min. For the determination of palladium, DDTT reagent is used and the precipitate is weighed as Pd $(C_{15}H_{10}N_3S)_2$ which contains 16·75% of palladium. For the determination of thallium, PDTT reagent is used and the precipitate is weighed as $TlC_9H_6N_3S$ which contains 52·00% of thallium.

RESULTS AND DISCUSSION

Solutions of the reagents in sodium hydroxide are stable indefinitely. The solid sodium salts of the reagents, recovered from aqueous sodium hydroxide solutions, were orange powders stable up to 360° and moderately soluble in chloroform. Analysis of the precipitates of the palladium and thallium complexes prepared according to the recommended gravimetric procedures are given in Table I and results of gravimetric determination of palladium(II) and thallium(I) are given in Table II.

TABLE I.—ANALYTICAL DATA OF PALLADIUM AND THALLIUM COMPLEXES

	C, %	H, %	N, %	S, %	Decomposition temperature, °*C*
Pd $(C_{15}H_{10}N_3S)_2$					
required	56·75	3·15	13·24	10·12	
found	56·7	3·2	13·3	10·0	248–250
Tl $C_9H_6N_3S$					
required	27·35	1·58	10·65	8·25	
found	27·3	1·6	10·6	8·2	150–152

TABLE II.—RESULTS OF DETERMINATION OF PALLADIUM AND THALLIUM

Pd taken, *mg*	Pd found, *mg*	Relative error %	Tl taken, *mg*	Tl found, *mg*	Relative error %
5·0	5·1	2	6·2	6·1	−2
11·3	11·2	−1	12·5	12·5	0
25·4	25·5	+0·4	25·0	25·1	+0·4
33·9	34·0	+0·3	37·5	37·4	−0·3

When cyanide was used as a masking agent DDTT still gave a yellow precipitate with thallium(I) in alkaline solution. The precipitation is specific but unsuitable for gravimetry because the precipitate has a low decomposition temperature (110–112°).

The precipitation of thallium(I) by PDTT and palladium(II) by DDTT is quantitative over the pH range 9–13. Both precipitates are yellow, crystalline, and non-hygroscopic and can easily be dried at 110°. The thermograms of the two metal complexes have been recorded (Fig. 1). Tl–PDTT (curve *a*) decomposes at temperatures above 150° and Pd–DDTT (curve *b*) is stable up to at least 240°. Pd(II)–DDTT complex is soluble in chloroform ($\varepsilon = 2{\cdot}3 \times 10^4$ l. mole^{-1}.cm^{-1} at 250 nm). An attempt to extract this complex into chloroform and measure it spectrophotometrically failed because the excess of reagent (λ_{max} = 315 nm in chloroform) is also extracted and causes non-reproducible results.

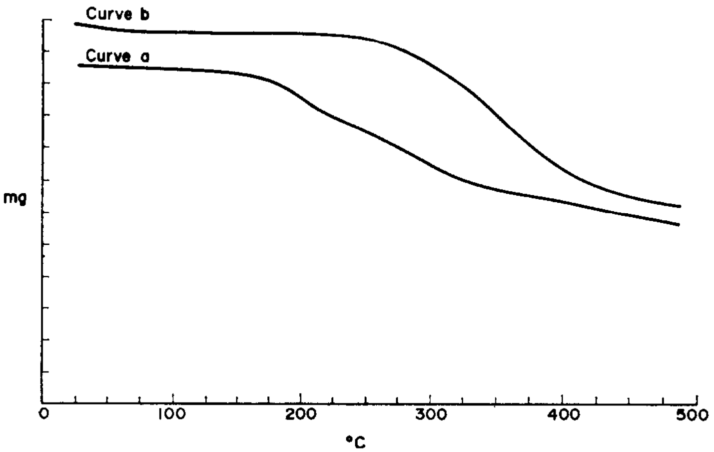


FIG. 1.—Thermograms of (*a*) Tl–PDTT; (*b*) Pd(II)–DDTT.

In the precipitation of palladium a 100-fold excess of Au(III), Bi, Cu(II), Fe(III), Pb, Co(II) and Ni give an error within ±2%. Sn(II) must be oxidized to Sn(IV) by addition of appropriate amounts of iron(III) chloride to prevent its hydrolysis in alkaline tartrate medium. Hg(II), Ag and Tl(I) will interfere in the gravimetric determination of palladium(II). The method is more sensitive than the dimethylglyoxime method. The precipitation of thallium as the PDTT complex is specific but less sensitive than the thionalide method.[3,4] In the presence of cyanide a 100-fold excess of Pd(II), Cu(II) or Ag did not cause significant error in the determination of thallium.

Department of Chemistry and Chemical Engineering M. EDRISSI
Teheran Polytechnique, Iran

Department of Chemistry, Pahlavi University A. MASSOUMI
Shiraz, Iran

Department of Chemistry, Faculty of Pharmacy I. LALEZARI
University of Teheran, Teheran, Iran

Summary—The analytical use of 6-phenyl-2,3-dihydro-*asym*-triazine-3-thione (PDTT) and 5,6-diphenyl-2,3-dihydro-*asym*-triazine-3-thione (DDTT) has been investigated. PDTT proved to be suitable for the

determination of thallium(I) in the presence of cyanide whereas DDTT is more selective than PDTT in alkaline tartrate solution and is applied for the selective gravimetric determination of palladium. The method is more sensitive than the dimethylglyoxime method. The only metal ions interfering are Hg(II), Ag and Tl(I).

Zusammenfassung—Die analytische Verwendbarkeit von 6-Phenyl-2,3-dihydro-*asym*-triazin-3-thion (PDTT) und 5,6-Diphenyl-2,3-dihydro-*asym*-triazin-3-thion (DDTT) wurde untersucht. PDTT ist zur Bestimmung von Thallium(I) in Gegenwart von Cyanid geeignet, DDTT ist in alkalischer Tartratlösung selektiver als PDTT und wird zur selektiven gravimetrischen Bestimmung von Palladium verwendet. Das Verfahren ist empfindlicher als das mit Dimethylglyoxim. An Metallionen stören nur Hg(II), Ag und Tl(I).

Résumé—On a étudié l'usage analytique de la 6-phényl 2,3-dihydro-*asym*-triazine 3-thione (PDTT) et de la 5,6-diphényl 2,3-dihydro-*asym*-triazine 3-thione (DDTT). La PDTT s'est avérée convenable pour le dosage du thallium(I) en la présence de cyanure, tandis que la DDTT est plus sélective que la PDTT en solution de tartrate alcalin et est appliquée au dosage gravimétrique sélectif du palladium. La méthode est plus sensible que la méthode à la diméthylglyoxime. Les seuls ions métalliques gênants sont Hg(II), Ag et Tl(I).

REFERENCES

1. I. Lalezari and H. Golgolab, *J. Heterocyclic Chem.*, 1970, **7**, 689.
2. M. Polonovski and M. Pesson, *Compt. Rend*, 1951, **232**, 1260.
3. I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part II, Volume 2, p. 60. Interscience, New York, 1962.
4. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., p. 549. Longmans, London, 1962.

Talanta, 1972, Vol. 19, pp. 817 to 821. Pergamon Press. Printed in Northern Ireland

Darstellung einer neuen Organoselenverbindung $(C_6H_5COCH_2)_4Se$, und ihre Anwendung zur Extraction von Selen. Bestimmung von Tellurspuren in reinem Selen

(*Eingegangen am* 5. *Juli* 1971. *Angenommen am* 2. *Dezember* 1971)

Es WERDEN organische Verbindungen des Selens mit gesättigten Monoketonen dargestellt—$(RCOCHR')_2SeCl_2$ (R und R' sind Alkyl- und Arylradikale)[1–8] die sich weder in Chloroform noch in Tetrachlorkohlenstoff oder Benzol leicht lösen, bedingt durch ihre polaren Charakter da sie leicht löslich sind in polaren Lösungsmitteln. Unser Ziel ist es, um die analytische Anwendung selenorganischen Verbindungen zu erweitern, polare Verbindungen darzustellen, die in Chloroform oder Tetrachlorkohlenstoff gut löslich sind, und die Extraktionsabtrennungen von großen Mengen Selens gewährleisten. Wir wählten also die vollständig organosubstituierte Verbindung des Typs $(RCOCHR')_4Se$ und verwendet Acetophenon als Ligand, da $(C_6H_5COCH_2)_2SeCl_2$ in festem Zustand mühelos erhalten wird und von uns besser erforscht ist.[7]

DARSTELLUNG UND EIGENSCHAFTEN VON $(C_6H_5COCH_2)_4Se$

Es werden 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3) in 20–25 ml 8,5*M* Salzsäure aufgelöst und 3 ml Acetophenon zugesetzt, entsprechend dem molaren Verhältnis Selen:Acetophenon = 1:4. Nach 1,5–2 Std. tritt das Selen in Verbindung quantitativ auf, als weißer Niederschlag der Zusammensetzung $(C_6H_5COCH_2)_2SeCl_2$.[6,7] Nach 350–400 stündigem Stehen wandelt sich der Niederschlag in ein gelb-grünes ölartiges Produkt um. Bei einem größeren Überschuß an Acetophenon steigt die Reaktionsgeschwindigkeit. Da unsere Versuche, mußte die Zusammensetzung des Produktes indirekt bestimmt werden. Als Kennzeichnungsmerkmal des Systems Selen–Acetophenon–Salzsäure wählten wir die Extrahierbarkeit der entstehenden Produkte durch Chloroform. Die Verteilung des Selens in den beiden Phasen ist in Abb. 1 angegeben.

determination of thallium(I) in the presence of cyanide whereas DDTT is more selective than PDTT in alkaline tartrate solution and is applied for the selective gravimetric determination of palladium. The method is more sensitive than the dimethylglyoxime method. The only metal ions interfering are Hg(II), Ag and Tl(I).

Zusammenfassung—Die analytische Verwendbarkeit von 6-Phenyl-2,3-dihydro-*asym*-triazin-3-thion (PDTT) und 5,6-Diphenyl-2,3-dihydro-*asym*-triazin-3-thion (DDTT) wurde untersucht. PDTT ist zur Bestimmung von Thallium(I) in Gegenwart von Cyanid geeignet, DDTT ist in alkalischer Tartratlösung selektiver als PDTT und wird zur selektiven gravimetrischen Bestimmung von Palladium verwendet. Das Verfahren ist empfindlicher als das mit Dimethylglyoxim. An Metallionen stören nur Hg(II), Ag und Tl(I).

Résumé—On a étudié l'usage analytique de la 6-phényl 2,3-dihydro-*asym*-triazine 3-thione (PDTT) et de la 5,6-diphényl 2,3-dihydro-*asym*-triazine 3-thione (DDTT). La PDTT s'est avérée convenable pour le dosage du thallium(I) en la présence de cyanure, tandis que la DDTT est plus sélective que la PDTT en solution de tartrate alcalin et est appliquée au dosage gravimétrique sélectif du palladium. La méthode est plus sensible que la méthode à la diméthylglyoxime. Les seuls ions métalliques gênants sont Hg(II), Ag et Tl(I).

REFERENCES

1. I. Lalezari and H. Golgolab, *J. Heterocyclic Chem.*, 1970, **7**, 689.
2. M. Polonovski and M. Pesson, *Compt. Rend*, 1951, **232**, 1260.
3. I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part II, Volume 2, p. 60. Interscience, New York, 1962.
4. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., p. 549. Longmans, London, 1962.

Talanta, 1972, Vol. 19, pp. 817 to 821. Pergamon Press. Printed in Northern Ireland

Darstellung einer neuen Organoselenverbindung $(C_6H_5COCH_2)_4Se$, und ihre Anwendung zur Extraction von Selen. Bestimmung von Tellurspuren in reinem Selen

(*Eingegangen am* 5. *Juli* 1971. *Angenommen am* 2. *Dezember* 1971)

Es WERDEN organische Verbindungen des Selens mit gesättigten Monoketonen dargestellt—$(RCOCHR')_2SeCl_2$ (R und R' sind Alkyl- und Arylradikale)$^{1-8}$ die sich weder in Chloroform noch in Tetrachlorkohlenstoff oder Benzol leicht lösen, bedingt durch ihre polaren Charakter da sie leicht löslich sind in polaren Lösungsmitteln. Unser Ziel ist es, um die analytische Anwendung selenorganischen Verbindungen zu erweitern, polare Verbindungen darzustellen, die in Chloroform oder Tetrachlorkohlenstoff gut löslich sind, und die Extraktionsabtrennungen von großen Mengen Selens gewährleisten. Wir wählten also die vollständig organosubstituierte Verbindung des Typs $(RCOCHR')_4Se$ und verwendet Acetophenon als Ligand, da $(C_6H_5COCH_2)_2SeCl_2$ in festem Zustand mühelos erhalten wird und von uns besser erforscht ist.^{7}

DARSTELLUNG UND EIGENSCHAFTEN VON $(C_6H_5COCH_2)_4Se$

Es werden 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3) in 20–25 ml 8,5*M* Salzsäure aufgelöst und 3 ml Acetophenon zugesetzt, entsprechend dem molaren Verhältnis Selen:Acetophenon = 1:4. Nach 1,5–2 Std. tritt das Selen in Verbindung quantitativ auf, als weißer Niederschlag der Zusammensetzung $(C_6H_5COCH_2)_2SeCl_2$.^{6,7} Nach 350–400 stündigem Stehen wandelt sich der Niederschlag in ein gelb-grünes ölartiges Produkt um. Bei einem größeren Überschuß an Acetophenon steigt die Reaktionsgeschwindigkeit. Da unsere Versuche, mußte die Zusammensetzung des Produktes indirekt bestimmt werden. Als Kennzeichnungsmerkmal des Systems Selen–Acetophenon–Salzsäure wählten wir die Extrahierbarkeit der entstehenden Produkte durch Chloroform. Die Verteilung des Selens in den beiden Phasen ist in Abb. 1 angegeben.

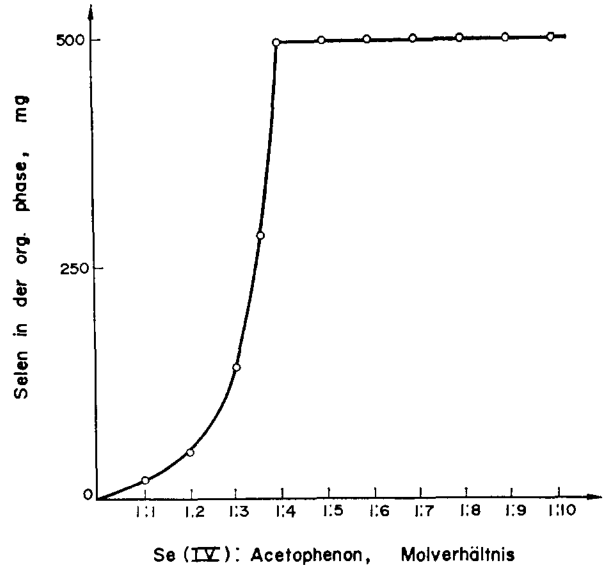


ABB. 1.—[HCl] = $9M$, ^{75}Se(IV)-Einwaage = 500 mg.

Es wurden versuche durchgeführt, wobei verschiedene Mengen an Acetophenon zu 25 ml $8{,}5M$ Salzsäure, die 500 mg Selen enthielten zugesetzt wurden. Nach 350 stündigem Stehen wurde das Selen in 10 ml Chloroform nach dreiminutigem Schütteln extrahiert. Der Gehalt an Selen wurde auch in den beiden Phasen bestimmt. Diese und alle folgenden Versuche wurden mit radioaktiven Selen-75 durchgeführt.

Um die molaren Verhältnisse, in denen die Komponenten reagieren, bestimmen zu können, muß man die Kinetik der Zusammenwirkung zwischen Selen und Acetophenon in salzsaurem Medium kennen. Die Ergebnisse von derartigen Versuchen sind in Abb. 2 dargestellt. Diese Versuche wurden bei denselben Bedingungen durchgeführt, wobei nur die Zeit des Stehens variiert wurde.

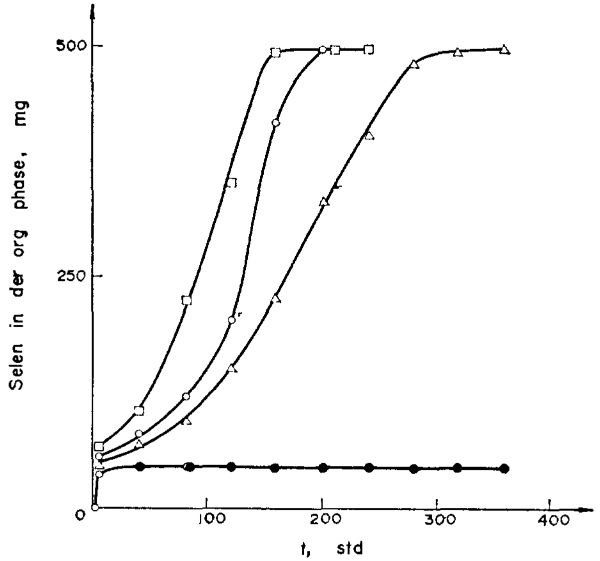


ABB. 2.—[HCl] = $9M$, ^{75}Se(IV)-Einwaage = 500 mg, molare Verhältnisse—● Selen:Acetophenon(I) = 1:2, △—Se:I = 1:4, ○—Se:I = 1:6, □—Se:I = 1:8.

Es wurde versucht Chloridionen in dem bei molarem Verhältnis Selen:Acetophenon größer als 1:4 erhaltenen ölartigen Produkt zu bestimmen. Zu diesem Zweck wurde das Produkt mehrmals mit Wasser gewaschen aber Chloridionen fand man nicht. Unter denselben Bedingungen wird das Chlor aus der Verbindung, die bei Verhältnis 1:2 erhalten wird und in großen Mengen Chloroform aufgelöst ist, mit Wasser quantitativ herausgewaschen. Die IR-Spektren, registriert aus flüssiger Schicht, zeigen, daß die Carbonylgruppe und der Benzolring in der erhaltenen Verbindung auf keine Weise beeinflußt sind. Bei 552 cm^{-1} wird eine für die C–Se Bindung charakteristische Absorption beobachtet. Die Ergebnisse von der Elementaranalyse sind: gefunden C 68,9%; H 5,4%; Se 14,1%, Cl 0,0%; gerechnet $[(C_6H_5COCH_2)_4Se]$ C 69,43%; H 5,07%; Se 14,21%, Cl 0,0%.

Das bis hier dargelegte läßt uns vermuten, daß $(C_6H_5COCH_2)_4Se$ die wahrscheinlichste Formel der erhaltenen Verbindung ist.

ANALYTISCHE ANWENDUNG VON $(C_6H_5COCH_2)_4Se$ ZUR ABTRENNUNG VON SELEN ALS MATRIXELEMENT

Das Extrahieren von großen Mengen an Selen gibt eine Möglichkeit für die analytische Bestimmung der Beimischungen, die das reine Selen begleiten und unter den beschriebenen Bedingungen in der wässrigen Phase zurückbleiben. Zu diesen Zweck war es notwendig, die Zeit zur Entstehung der selenorganischen Verbindung zu verkürzen.

Die Untersuchungen führten wir unter Erwärmung im Wasserbad in Gegenwart von Salzsäure oder einem Gemisch aus Salz- und Schwefelsäure durch. Der Einfluß der Schwefelsäure mußte untersucht werden, weil sie beim Auflösen reines Selens in Salpetersäure als Denitrierungsmittel verwendet wird und in der Lösung immer anwesend ist. Die Versuche zur Darstellung der Verbindung führten wir durch, indem wir zu 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3), aufgelöst in 25 ml Salzsäure verschiedener Konzentration, unter Schütteln Acetophenon zusetzten. Die Menge an Acetophenon entsprach dem molaren Verhältnis Selen:Acetophenon = 1:2. Nach ungefähr 1,5 Std bindet sich das Selen quantitativ und fällt in Form eines weißen Niederschlages aus. Die Lösung über dem Niederschlag muß klar sein. Man gibt noch zwei molare Teile Acetophenon unter periodischem Schütteln hinzu und erwärmt im Wasserbad. Die Zeit zur Entstehung der bei verschiedenen Temperaturen und Konzentrationen der Salzsäure dargestellten Verbindung ist in Tabelle I angegeben. Ein Maß für die Entstehung der Verbindung war ihre völlige Extraktion aus der wässrigen Phase in das Chloroform.

Analoge Versuche führten wir auch in Anwesenheit von $3N$ Schwefelsäure durch. Die Ergebnisse sind in Tabelle II angegeben.

TABELLE I.—REAKTIONSGESCHWINDIGKEIT IN SALZSAURE

[HCl], *M*	Zeit zur Entstehung der Verbindung, *Std*, bei Reaktionstemperatur 60–65°C	80–85°C	siedendes Wasserbad
5,0	2,5–3	1–1,5	0,85–1
5,5	2–2,5	1–1,5	0,85–1
6	1,5–2	0,7–1	0,5–0,75
7	1–1,5	0,45–0,5	0,25–0,40
8	0,75–1	zersetzt sich	zersetzt sich
9	0,75–1	zersetzt sich	zersetzt sich
10	0,75–1	zersetzt sich	zersetzt sich

TABELLE II.—REAKTIONSGESCHWINDIGKEIT IN GEMISCHTEN SÄUREN

Gesamtkonzentration von HCl + H_2SO_4 *N*	Zeit zur Entstehung der Verbindung, *Std*, bei Reaktionstemperatur 60–65°C	siedendes Wasserbad
4	8–9	5–6
6	3,5–4	4–5
7	0,75–1	1,5–2
8	0,75–1	0,5–0,70
9	1	zersetzt sich
10	1	zersetzt sich
11	1	zersetzt sich

Festgestellt wurde, daß die Verbindung bei 5*M* Salzsäure und 3*N* Schwefelsäure und Erwärmung im Wasserbad im Laufe einer Stunde bei 60–65° entsteht. Danach wird mit 5 ml Chloroform oder Tetrachlorkohlenstoff extrahiert. Das Selen geht in die organische Phase quantitativ über. Unter den beschriebenen Bedingungen geht neben Selen auch Gold(III) in die organische Phase über. Das letztere wird durch verdünnte Salzsäure nicht zurückextrahiert. In der wässrigen Phase bleiben folgende Metallionen zurück: Ru(IV), Rh(IV), Os(IV), Ir(IV), Pt(IV), Pd(II), Te(IV), Cu(II). Das Verhalten von Gold(III) wird Gegenstand weiterer Untersuchungen sein. Die erhaltenen Ergebnisse wurden zur Bestimmung von Tellur in reinem Selen benutzt.

ANWENDUNG DER METHODE ZUR BESTIMMUNG VON TELLUR IN REINEM SELEN

Zur Bestimmung von Tellur, das nach der Abtrennung von Selen in der wässrigen Phase zurückbleibt, beschlossen wir die bekannte photometrische Methode anzuwenden, die auf der Messung der Extinktion von Kolloidlösungen von elementarem Tellur, erhalten durch Reduktion mit Zinn(II)-chlorid, beruht.[9–11] Die Ergebnisse zeigten, daß folgende Elemente in den angegebenen Mengen (in 50 ml) die Photometrische Bestimmung von Tellur nicht stören: Pd(II)—5 μg, Au(III)—15 μg, Os(IV)—19 μg, Ru(IV)—13 μg, Ir(IV)—19 μg, Pt(IV)—6 μg.

Reagenzien

Konz. HCl, H_2SO_4 und HNO_3 *p.a.*
Lösung von $SnCl_2$, 25%-ige.
Lösung von Gelatine, 0,5%-ige.
Acetophenon *p.a.*

Es werden 0,2–3 g Selen in 5–15 ml konz. Salpetersäure aufgelöst. Die Probe die 20–200 μg Tellur enthalten soll wird im Wasserbad erwärmt, bis sich das Volumen auf 2–3 ml verringert. Man setzt 2,5 ml konz. Schwefelsäure und 2–3 ml Wasser hinzu und erwärmt weiter auf 250–300° im Sandbad bis zur Entstehung von SO_3. Man setzt noch Wasser und Salzsäure so zu, daß das Gesamtvolumen 25 ml und die Konzentration an Salzsäure 5*M* wird. Dann werden pro molaren Teil Selen vier molaren Teile Acetophenon zugesetzt. Zuerst gibt man unter heftigem Schütteln die Hälfte von der berechneten Menge an Acetophenon zu. Nach 1,5 Std wird die andere Hälfte zugegeben. Es wird im Wasserbad bei 60–65° eine Stunde lang erwärmt, wobei man in Zeitabständen schüttelt. Die Lösung muß völlig klar sein. Die Probe wird in einem Schütteltrichter gegeben und mit 8 ml Chloroform oder Tetrachlorkohlenstoff 2 min lang extrahiert. Die wässrige Phase wird filtriert und in einen 50 ml Meßkolben versetzt. Die organische Phase wird mit 5 ml 2*M* Salzsäure 20–30 sec lang gewaschen und die salzsaure Lösung der wässrigen Phase zugesetzt. Die Gesamtmenge in dem Meßkolben wird auf 40 ml gebrucht. Man kühlt auf 20° ab und setzt 0,5 ml $SnCl_2$-Lösung zu. Es wird geschüttelt und 5 min stehengelassen; man gibt noch 3 ml Gelatine-Lösung hinzu, verdünnt nach 10 min auf 50 ml und mißt die Extinktion bei 434 nm in einer 50-mm Küvette. Die Standartgraphik wird für Mengen von 20–200 μg pro 50 ml aufgezeichnet.

Um uns zu überzeugen, daß keine Verlußte an Tellur beim Auflösen und Abtrennen des Selens entstehen, setzten wir verschiedenen Mengen reinen Selens (0,5, 1, 2, 3 g) 50 μg Te zu. Die Proben wurden nach der Analysenvorschrift bearbeitet. Die Ergebnisse sind statistisch bearbeitet worden.

$$N = 10 \qquad \bar{x} = 50{,}0\,\mu\text{g} \qquad s = 1{,}19\,\mu\text{g} \qquad V = \frac{s}{\bar{x}} \cdot t \cdot 100 = 5{,}4\%$$
$$\text{bei } P = 95 \qquad t = 2{,}26$$

Wir geben auch die statistischen Ergebnisse von der Bestimmung von 50 μg Te unter reinen Bedingungen an.

$$N = 10 \qquad \bar{x} = 49{,}8\,\mu\text{g} \qquad s = 1{,}22\,\mu\text{g} \qquad V = \frac{s}{\bar{x}} \cdot t \cdot 100 = 5{,}3\%$$
$$\text{bei } P = 95 \qquad t = 2{,}26$$

DISKUSSION

Eine frühere Arbeit[6] befaßte sich mit der Extraktion von 5–25 μg Selen. Während in jenem Falle die begrenzte Löslichkeit von $(C_6H_5COCH_2)_2SeCl_2$ keine Schwierigkeiten bot, wird die Extraktion von großen Mengen Selen nur möglich sein, wenn die Selenverbindung in Chloroform praktisch unbegrenzt löslich ist, das bei $(C_6H_5COCH_2)_4Se$ der Fall ist. Da andere Elemente wie Te(IV), Au(III) nur als Ionenassoziate extrahiert werden, sind sie auch leight zurückzuextrahieren und daher von Selen abzutrennen, wie in vorliegender Arbeit am Beispiel von Tellurbestimmung aufgezeigt wird.

Höheres Pädagogisches Institut
Plovdiv
Bulgarien

L. Futekov
B. Atanasova

Zusammenfassung—Erhalten wurde eine neue Verbindung von Se(IV) mit Acetophenon in salzsaurem Medium, $(C_6H_5COCH_2)_4Se$. Der Prozeß der Entstehung der Verbindung dauert beim Überschuß an Acetophenon (Selen:Acetophenon $<$ 1:4) ungefähr 300–400 Std, aber bei 60–70° nur 1,5–2 Std. Die erhaltene Verbindung löst sich sehr gut in Chloroform und Tetrachlorkohlenstoff. Diese Eigenschaft wird zur Extraktionsabtrennung von großen Mengen an Selen benutzt. Auf diese Weise wird eine gute Möglichkeit zur Bestimmung von Beimischungen in reinem Selen gegeben. Die Methode ist zur Bestimmung von Tellur in Selen angewandt worden.

Summary—A new compound has been prepared from Se(IV) and acetophenone in hydrochloric acid solution. At 60–70° conversion into $(C_6H_5COCH_2)_4Se$ is complete in 1·5–2 hr. The product is very soluble in chloroform and in carbon tetrachloride and thus offers a possibility for the separation of large quantities of selenium before determination of impurities in it. The method has been applied to the separation and determination of traces of tellurium in selenium.

Résumé—On a préparé un nouveau composé à partir de Se(IV) et d'acétophénone en solution dans l'acide chlorhydrique. A 60–70°, la conversion en $(C_6H_5COCH_2)_4Se$ est complète en 1,5–2 h. Le produit est très soluble en chloroforme et en tétrachlorure de carbone et offre ainsi une possibilité de séparation de grandes quantités de sélénium avant détermination des impuretés qu'il contient. On a appliqué la méthode à la séparation et au dosage de traces de tellurium dans le sélénium.

LITERATUR

1. N. Jordanov und L. Futekov, *Nachrichten Inst Allg. Anorg. Chemie, BAW*, 1966, **4**, 25.
2. L. Futekov und N. Jordanov, *Nachrichten Abt. Chemie, BAW*, 1968, **I**, **4**, 157.
3. N. Jordanov und L. Futekov, *Talanta*, 1965, **12**, 371.
4. *Idem*, *ibid.*, 1966, **13**, 163.
5. L. Futekov und N. Jordanov, *ibid.*, 1966, **13**, 763.
6. N. Jordanov und L. Futekov, *ibid.*, 1968, **15**, 850.
7. L. Futekov, N. Jordanov und A. Georgieva, *Natura*, 1968, **II**, **I**, 59.
8. L. Futekov und B. Atanasova, *ibid*, 1970, **III**, **I**, 65.
9. S. Wolkov, *Zavodsk. Lab.*, 1936, **5**, 1429.
10. W. Semel, *ibid.*, 1936, **5**, 1433.
11. P. Crossley, *Analyst*, 1944, **69**, 206.

Talanta, 1972, Vol. 19, pp. 821 to 824. Pergamon Press. Printed in Northern Ireland

Détermination de l'or par réaction d'échange de complexes triples à association ionique

(*Reçu le* 31 *Mars* 1971. *Accepté le* 2 *Octobre* 1971)

De nombreux anions du type [ML_4], réagissant avec certains agents organiques de nature basique, fournissent des composés ordinairement peu solubles dans l'eau, mais extractibles dans des solvants organiques appropriés.

Lorsque l'agent organique—base —est un colorant, on est en présence de réactions à sensibilité élevée, mais généralement à faible sélectivité. D'autre part, les réactions de ces mêmes anions [ML_4^-] avec certains agents à basicité plus prononcée, mais incolores, se distinguent par leur haute sélectivité et leur faible sensibilité.

L'usage combiné de ces deux espèces de réactions permet de créer des méthodes sensibles et en même temps suffisamment sélectives.

determination of thallium(I) in the presence of cyanide whereas DDTT is more selective than PDTT in alkaline tartrate solution and is applied for the selective gravimetric determination of palladium. The method is more sensitive than the dimethylglyoxime method. The only metal ions interfering are Hg(II), Ag and Tl(I).

Zusammenfassung—Die analytische Verwendbarkeit von 6-Phenyl-2,3-dihydro-*asym*-triazin-3-thion (PDTT) und 5,6-Diphenyl-2,3-dihydro-*asym*-triazin-3-thion (DDTT) wurde untersucht. PDTT ist zur Bestimmung von Thallium(I) in Gegenwart von Cyanid geeignet, DDTT ist in alkalischer Tartratlösung selektiver als PDTT und wird zur selektiven gravimetrischen Bestimmung von Palladium verwendet. Das Verfahren ist empfindlicher als das mit Dimethylglyoxim. An Metallionen stören nur Hg(II), Ag und Tl(I).

Résumé—On a étudié l'usage analytique de la 6-phényl 2,3-dihydro-*asym*-triazine 3-thione (PDTT) et de la 5,6-diphényl 2,3-dihydro-*asym*-triazine 3-thione (DDTT). La PDTT s'est avérée convenable pour le dosage du thallium(I) en la présence de cyanure, tandis que la DDTT est plus sélective que la PDTT en solution de tartrate alcalin et est appliquée au dosage gravimétrique sélectif du palladium. La méthode est plus sensible que la méthode à la diméthylglyoxime. Les seuls ions métalliques gênants sont Hg(II), Ag et Tl(I).

REFERENCES

1. I. Lalezari and H. Golgolab, *J. Heterocyclic Chem.*, 1970, **7**, 689.
2. M. Polonovski and M. Pesson, *Compt. Rend*, 1951, **232**, 1260.
3. I. M. Kolthoff and P. J. Elving, eds., *Treatise on Analytical Chemistry*, Part II, Volume 2, p. 60. Interscience, New York, 1962.
4. A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., p. 549. Longmans, London, 1962.

Talanta, 1972, Vol. 19, pp. 817 to 821. Pergamon Press. Printed in Northern Ireland

Darstellung einer neuen Organoselenverbindung $(C_6H_5COCH_2)_4Se$, und ihre Anwendung zur Extraction von Selen. Bestimmung von Tellurspuren in reinem Selen

(*Eingegangen am* 5. *Juli* 1971. *Angenommen am* 2. *Dezember* 1971)

Es WERDEN organische Verbindungen des Selens mit gesättigten Monoketonen dargestellt—$(RCOCHR')_2SeCl_2$ (R und R′ sind Alkyl- und Arylradikale)$^{1-8}$ die sich weder in Chloroform noch in Tetrachlorkohlenstoff oder Benzol leicht lösen, bedingt durch ihre polaren Charakter da sie leicht löslich sind in polaren Lösungsmitteln. Unser Ziel ist es, um die analytische Anwendung selenorganischen Verbindungen zu erweitern, polare Verbindungen darzustellen, die in Chloroform oder Tetrachlorkohlenstoff gut löslich sind, und die Extraktionsabtrennungen von großen Mengen Selens gewährleisten. Wir wählten also die vollständig organosubstituierte Verbindung des Typs $(RCOCHR')_4Se$ und verwendet Acetophenon als Ligand, da $(C_6H_5COCH_2)_2SeCl_2$ in festem Zustand mühelos erhalten wird und von uns besser erforscht ist.^{7}

DARSTELLUNG UND EIGENSCHAFTEN VON $(C_6H_5COCH_2)_4Se$

Es werden 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3) in 20–25 ml 8,5*M* Salzsäure aufgelöst und 3 ml Acetophenon zugesetzt, entsprechend dem molaren Verhältnis Selen:Acetophenon = 1:4. Nach 1,5–2 Std. tritt das Selen in Verbindung quantitativ auf, als weißer Niederschlag der Zusammensetzung $(C_6H_5COCH_2)_2SeCl_2$.^{6,7} Nach 350–400 stündigem Stehen wandelt sich der Niederschlag in ein gelb-grünes ölartiges Produkt um. Bei einem größeren Überschuß an Acetophenon steigt die Reaktionsgeschwindigkeit. Da unsere Versuche, mußte die Zusammensetzung des Produktes indirekt bestimmt werden. Als Kennzeichnungsmerkmal des Systems Selen–Acetophenon–Salzsäure wählten wir die Extrahierbarkeit der entstehenden Produkte durch Chloroform. Die Verteilung des Selens in den beiden Phasen ist in Abb. 1 angegeben.

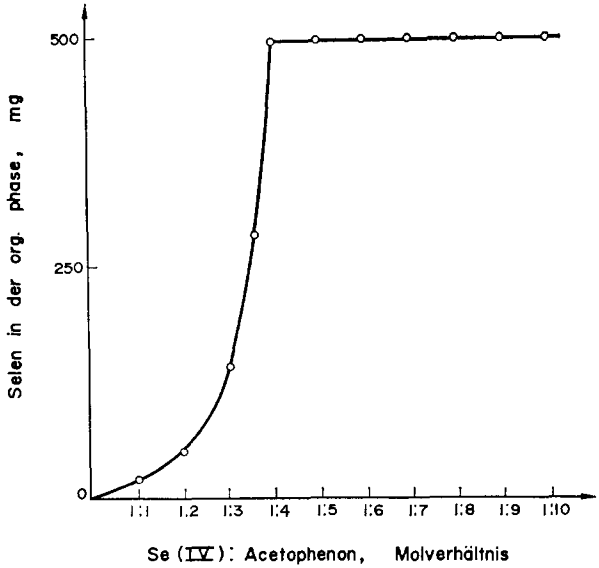


Abb. 1.—[HCl] = $9M$, ^{75}Se(IV)-Einwaage = 500 mg.

Es wurden versuche durchgeführt, wobei verschiedene Mengen an Acetophenon zu 25 ml $8,5M$ Salzsäure, die 500 mg Selen enthielten zugesetzt wurden. Nach 350 stündigem Stehen wurde das Selen in 10 ml Chloroform nach dreiminutigem Schütteln extrahiert. Der Gehalt an Selen wurde auch in den beiden Phasen bestimmt. Diese und alle folgenden Versuche wurden mit radioaktiven Selen-75 durchgeführt.

Um die molaren Verhältnisse, in denen die Komponenten reagieren, bestimmen zu können, muß man die Kinetik der Zusammenwirkung zwischen Selen und Acetophenon in salzsaurem Medium kennen. Die Ergebnisse von derartigen Versuchen sind in Abb. 2 dargestellt. Diese Versuche wurden bei denselben Bedingungen durchgeführt, wobei nur die Zeit des Stehens variiert wurde.

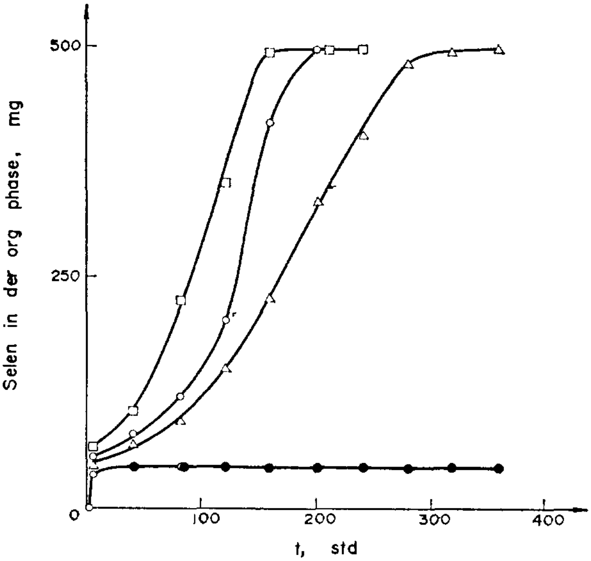


Abb. 2.—[HCl] = $9M$, ^{75}Se(IV)-Einwaage = 500 mg, molare Verhältnisse—● Selen:Acetophenon(I) = 1:2, △—Se:I = 1:4, ○—Se:I = 1:6, □—Se:I = 1:8.

Es wurde versucht Chloridionen in dem bei molarem Verhältnis Selen:Acetophenon größer als 1:4 erhaltenen ölartigen Produkt zu bestimmen. Zu diesem Zweck wurde das Produkt mehrmals mit Wasser gewaschen aber Chloridionen fand man nicht. Unter denselben Bedingungen wird das Chlor aus der Verbindung, die bei Verhältnis 1:2 erhalten wird und in großen Mengen Chloroform aufgelöst ist, mit Wasser quantitativ herausgewaschen. Die IR-Spektren, registriert aus flüssiger Schicht, zeigen, daß die Carbonylgruppe und der Benzolring in der erhaltenen Verbindung auf keine Weise beeinflußt sind. Bei 552 cm^{-1} wird eine für die C–Se Bindung charakteristische Absorption beobachtet. Die Ergebnisse von der Elementaranalyse sind: gefunden C 68,9%; H 5,4%; Se 14,1%, Cl 0,0%; gerechnet $[(C_6H_5COCH_2)_4Se]$ C 69,43%; H 5,07%; Se 14,21%, Cl 0,0%.

Das bis hier dargelegte läßt uns vermuten, daß $(C_6H_5COCH_2)_4Se$ die wahrscheinlichste Formel der erhaltenen Verbindung ist.

ANALYTISCHE ANWENDUNG VON $(C_6H_5COCH_2)_4Se$ ZUR ABTRENNUNG VON SELEN ALS MATRIXELEMENT

Das Extrahieren von großen Mengen an Selen gibt eine Möglichkeit für die analytische Bestimmung der Beimischungen, die das reine Selen begleiten und unter den beschriebenen Bedingungen in der wässrigen Phase zurückbleiben. Zu diesen Zweck war es notwendig, die Zeit zur Entstehung der selenorganischen Verbindung zu verkürzen.

Die Untersuchungen führten wir unter Erwärmung im Wasserbad in Gegenwart von Salzsäure oder einem Gemisch aus Salz- und Schwefelsäure durch. Der Einfluß der Schwefelsäure mußte untersucht werden, weil sie beim Auflösen reines Selens in Salpetersäure als Denitrierungsmittel verwendet wird und in der Lösung immer anwesend ist. Die Versuche zur Darstellung der Verbindung führten wir durch, indem wir zu 0,5 g Selen (in Form von SeO_2 oder H_2SeO_3), aufgelöst in 25 ml Salzsäure verschiedener Konzentration, unter Schütteln Acetophenon zusetzten. Die Menge an Acetophenon entsprach dem molaren Verhältnis Selen:Acetophenon = 1:2. Nach ungefähr 1,5 Std bindet sich das Selen quantitativ und fällt in Form eines weißen Niederschlages aus. Die Lösung über dem Niederschlag muß klar sein. Man gibt noch zwei molare Teile Acetophenon unter periodischem Schütteln hinzu und erwärmt im Wasserbad. Die Zeit zur Entstehung der bei verschiedenen Temperaturen und Konzentrationen der Salzsäure dargestellten Verbindung ist in Tabelle I angegeben. Ein Maß für die Entstehung der Verbindung war ihre völlige Extraktion aus der wässrigen Phase in das Chloroform.

Analoge Versuche führten wir auch in Anwesenheit von 3*N* Schwefelsäure durch. Die Ergebnisse sind in Tabelle II angegeben.

TABELLE I.—REAKTIONSGESCHWINDIGKEIT IN SALZSAURE

	Zeit zur Entstehung der Verbindung, *Std*, bei Reaktionstemperatur		
[HCl], *M*	60–65°C	80–85°C	siedendes Wasserbad
5,0	2,5–3	1–1,5	0,85–1
5,5	2–2,5	1–1,5	0,85–1
6	1,5–2	0,7–1	0,5–0,75
7	1–1,5	0,45–0,5	0,25–0,40
8	0,75–1	zersetzt sich	zersetzt sich
9	0,75–1	zersetzt sich	zersetzt sich
10	0,75–1	zersetzt sich	zersetzt sich

TABELLE II.—REAKTIONSGESCHWINDIGKEIT IN GEMISCHTEN SÄUREN

Gesamtkonzentration von HCl + H_2SO_4	Zeit zur Entstehung der Verbindung, *Std*, bei Reaktionstemperatur	
N	60–65°C	siedendes Wasserbad
4	8–9	5–6
6	3,5–4	4–5
7	0,75–1	1,5–2
8	0,75–1	0,5–0,70
9	1	zersetzt sich
10	1	zersetzt sich
11	1	zersetzt sich

Festgestellt wurde, daß die Verbindung bei $5M$ Salzsäure und $3N$ Schwefelsäure und Erwärmung im Wasserbad im Laufe einer Stunde bei 60–65° entsteht. Danach wird mit 5 ml Chloroform oder Tetrachlorkohlenstoff extrahiert. Das Selen geht in die organische Phase quantitativ über. Unter den beschriebenen Bedingungen geht neben Selen auch Gold(III) in die organische Phase über. Das letztere wird durch verdünnte Salzsäure nicht zurückextrahiert. In der wässrigen Phase bleiben folgende Metallionen zurück: Ru(IV), Rh(IV), Os(IV), Ir(IV), Pt(IV), Pd(II), Te(IV), Cu(II). Das Verhalten von Gold(III) wird Gegenstand weiterer Untersuchungen sein. Die erhaltenen Ergebnisse wurden zur Bestimmung von Tellur in reinem Selen benutzt.

ANWENDUNG DER METHODE ZUR BESTIMMUNG VON TELLUR IN REINEM SELEN

Zur Bestimmung von Tellur, das nach der Abtrennung von Selen in der wässrigen Phase zurückbleibt, beschlossen wir die bekannte photometrische Methode anzuwenden, die auf der Messung der Extinktion von Kolloidlösungen von elementarem Tellur, erhalten durch Reduktion mit Zinn(II)-chlorid, beruht.[9–11] Die Ergebnisse zeigten, daß folgende Elemente in den angegebenen Mengen (in 50 ml) die Photometrische Bestimmung von Tellur nicht stören: Pd(II)—5 μg, Au(III)—15 μg, Os(IV)—19 μg, Ru(IV)—13 μg, Ir(IV)—19 μg, Pt(IV)—6 μg.

Reagenzien

Konz. HCl, H_2SO_4 und HNO_3 *p.a.*
Lösung von $SnCl_2$, 25 %-ige.
Lösung von Gelatine, 0,5 %-ige.
Acetophenon *p.a.*

Es werden 0,2–3 g Selen in 5–15 ml konz. Salpetersäure aufgelöst. Die Probe die 20–200 μg Tellur enthalten soll wird im Wasserbad erwärmt, bis sich das Volumen auf 2–3 ml verringert. Man setzt 2,5 ml konz. Schwefelsäure und 2–3 ml Wasser hinzu und erwärmt weiter auf 250–300° im Sandbad bis zur Entstehung von SO_3. Man setzt noch Wasser und Salzsäure so zu, daß das Gesamtvolumen 25 ml und die Konzentration an Salzsäure $5M$ wird. Dann werden pro molaren Teil Selen vier molaren Teile Acetophenon zugesetzt. Zuerst gibt man unter heftigem Schütteln die Hälfte von der berechneten Menge an Acetophenon zu. Nach 1,5 Std wird die andere Hälfte zugegeben. Es wird im Wasserbad bei 60–65° eine Stunde lang erwärmt, wobei man in Zeitabständen schüttelt. Die Lösung muß völlig klar sein. Die Probe wird in einem Schütteltrichter gegeben und mit 8 ml Chloroform oder Tetrachlorkohlenstoff 2 min lang extrahiert. Die wässrige Phase wird filtriert und in einen 50 ml Meßkolben versetzt. Die organische Phase wird mit 5 ml $2M$ Salzsäure 20–30 sec lang gewaschen und die salzsaure Lösung der wässrigen Phase zugesetzt. Die Gesamtmenge in dem Meßkolben wird auf 40 ml gebrucht. Man kühlt auf 20° ab und setzt 0,5 ml $SnCl_2$-Lösung zu. Es wird geschüttelt und 5 min stehengelassen; man gibt noch 3 ml Gelatine-Lösung hinzu, verdünnt nach 10 min auf 50 ml und mißt die Extinktion bei 434 nm in einer 50-mm Küvette. Die Standartgraphik wird für Mengen von 20–200 μg pro 50 ml aufgezeichnet.

Um uns zu überzeugen, daß keine Verlußte an Tellur beim Auflösen und Abtrennen des Selens entstehen, setzten wir verschiedenen Mengen reinen Selens (0,5, 1, 2, 3 g) 50 μg Te zu. Die Proben wurden nach der Analysenvorschrift bearbeitet. Die Ergebnisse sind statistisch bearbeitet worden.

$$N = 10 \quad \bar{x} = 50{,}0\,\mu g \quad s = 1{,}19\,\mu g \quad V = \frac{s}{\bar{x}} \cdot t \cdot 100 = 5{,}4\%$$
$$\text{bei } P = 95 \quad t = 2{,}26$$

Wir geben auch die statistischen Ergebnisse von der Bestimmung von 50 μg Te unter reinen Bedingungen an.

$$N = 10 \quad \bar{x} = 49{,}8\,\mu g \quad s = 1{,}22\,\mu g \quad V = \frac{s}{\bar{x}} \cdot t \cdot 100 = 5{,}3\,\%$$
$$\text{bei } P = 95 \quad t = 2{,}26$$

DISKUSSION

Eine frühere Arbeit[6] befaßte sich mit der Extraktion von 5–25 μg Selen. Während in jenem Falle die begrenzte Löslichkeit von $(C_6H_5COCH_2)_2SeCl_2$ keine Schwierigkeiten bot, wird die Extraktion von großen Mengen Selen nur möglich sein, wenn die Selenverbindung in Chloroform praktisch unbegrenzt löslich ist, das bei $(C_6H_5COCH_2)_4Se$ der Fall ist. Da andere Elemente wie Te(IV), Au(III) nur als Ionenassoziate extrahiert werden, sind sie auch leight zurückzuextrahieren und daher von Selen abzutrennen, wie in vorliegender Arbeit am Beispiel von Tellurbestimmung aufgezeigt wird.

Höheres Pädagogisches Institut
Plovdiv
Bulgarien

L. Futekov
B. Atanasova

Zusammenfassung—Erhalten wurde eine neue Verbindung von Se(IV) mit Acetophenon in salzsaurem Medium, $(C_6H_5COCH_2)_4Se$. Der Prozeß der Entstehung der Verbindung dauert beim Überschuß an Acetophenon (Selen:Acetophenon < 1:4) ungefähr 300–400 Std, aber bei 60–70° nur 1,5–2 Std. Die erhaltene Verbindung löst sich sehr gut in Chloroform und Tetrachlorkohlenstoff. Diese Eigenschaft wird zur Extraktionsabtrennung von großen Mengen an Selen benutzt. Auf diese Weise wird eine gute Möglichkeit zur Bestimmung von Beimischungen in reinem Selen gegeben. Die Methode ist zur Bestimmung von Tellur in Selen angewandt worden.

Summary—A new compound has been prepared from Se(IV) and acetophenone in hydrochloric acid solution. At 60–70° conversion into $(C_6H_5COCH_2)_4Se$ is complete in 1·5–2 hr. The product is very soluble in chloroform and in carbon tetrachloride and thus offers a possibility for the separation of large quantities of selenium before determination of impurities in it. The method has been applied to the separation and determination of traces of tellurium in selenium.

Résumé—On a préparé un nouveau composé à partir de Se(IV) et d'acétophénone en solution dans l'acide chlorhydrique. A 60–70°, la conversion en $(C_6H_5COCH_2)_4Se$ est complète en 1,5–2 h. Le produit est très soluble en chloroforme et en tétrachlorure de carbone et offre ainsi une possibilité de séparation de grandes quantités de sélénium avant détermination des impuretés qu'il contient. On a appliqué la méthode à la séparation et au dosage de traces de tellurium dans le sélénium.

LITERATUR

1. N. Jordanov und L. Futekov, *Nachrichten Inst Allg. Anorg. Chemie, BAW*, 1966, **4**, 25.
2. L. Futekov und N. Jordanov, *Nachrichten Abt. Chemie, BAW*, 1968, **I**, **4**, 157.
3. N. Jordanov und L. Futekov, *Talanta*, 1965, **12**, 371.
4. *Idem*, *ibid.*, 1966, **13**, 163.
5. L. Futekov und N. Jordanov, *ibid.*, 1966, **13**, 763.
6. N. Jordanov und L. Futekov, *ibid.*, 1968, **15**, 850.
7. L. Futekov, N. Jordanov und A. Georgieva, *Natura*, 1968, **II**, **I**, 59.
8. L. Futekov und B. Atanasova, *ibid*, 1970, **III**, **I**, 65.
9. S. Wolkov, *Zavodsk. Lab.*, 1936, **5**, 1429.
10. W. Semel, *ibid.*, 1936, **5**, 1433.
11. P. Crossley, *Analyst*, 1944, **69**, 206.

Talanta, 1972, Vol. 19, pp. 821 to 824. Pergamon Press. Printed in Northern Ireland

Détermination de l'or par réaction d'échange de complexes triples à association ionique

(*Reçu le* 31 *Mars* 1971. *Accepté le* 2 *Octobre* 1971)

De nombreux anions du type $[ML_4]$, réagissant avec certains agents organiques de nature basique, fournissent des composés ordinairement peu solubles dans l'eau, mais extractibles dans des solvants organiques appropriés.

Lorsque l'agent organique—base —est un colorant, on est en présence de réactions à sensibilité élevée, mais généralement à faible sélectivité. D'autre part, les réactions de ces mêmes anions $[ML_4^-]$ avec certains agents à basicité plus prononcée, mais incolores, se distinguent par leur haute sélectivité et leur faible sensibilité.

L'usage combiné de ces deux espèces de réactions permet de créer des méthodes sensibles et en même temps suffisamment sélectives.

Zusammenfassung—Erhalten wurde eine neue Verbindung von Se(IV) mit Acetophenon in salzsaurem Medium, $(C_6H_5COCH_2)_4Se$. Der Prozeß der Entstehung der Verbindung dauert beim Überschuß an Acetophenon (Selen:Acetophenon $<$ 1:4) ungefähr 300–400 Std, aber bei 60–70° nur 1,5–2 Std. Die erhaltene Verbindung löst sich sehr gut in Chloroform und Tetrachlorkohlenstoff. Diese Eigenschaft wird zur Extraktionsabtrennung von großen Mengen an Selen benutzt. Auf diese Weise wird eine gute Möglichkeit zur Bestimmung von Beimischungen in reinem Selen gegeben. Die Methode ist zur Bestimmung von Tellur in Selen angewandt worden.

Summary—A new compound has been prepared from Se(IV) and acetophenone in hydrochloric acid solution. At 60–70° conversion into $(C_6H_5COCH_2)_4Se$ is complete in 1·5–2 hr. The product is very soluble in chloroform and in carbon tetrachloride and thus offers a possibility for the separation of large quantities of selenium before determination of impurities in it. The method has been applied to the separation and determination of traces of tellurium in selenium.

Résumé—On a préparé un nouveau composé à partir de Se(IV) et d'acétophénone en solution dans l'acide chlorhydrique. A 60–70°, la conversion en $(C_6H_5COCH_2)_4Se$ est complète en 1,5–2 h. Le produit est très soluble en chloroforme et en tétrachlorure de carbone et offre ainsi une possibilité de séparation de grandes quantités de sélénium avant détermination des impuretés qu'il contient. On a appliqué la méthode à la séparation et au dosage de traces de tellurium dans le sélénium.

LITERATUR

1. N. Jordanov und L. Futekov, *Nachrichten Inst Allg. Anorg. Chemie, BAW*, 1966, **4**, 25.
2. L. Futekov und N. Jordanov, *Nachrichten Abt. Chemie, BAW*, 1968, **I**, **4**, 157.
3. N. Jordanov und L. Futekov, *Talanta*, 1965, **12**, 371.
4. *Idem*, *ibid.*, 1966, **13**, 163.
5. L. Futekov und N. Jordanov, *ibid.*, 1966, **13**, 763.
6. N. Jordanov und L. Futekov, *ibid.*, 1968, **15**, 850.
7. L. Futekov, N. Jordanov und A. Georgieva, *Natura*, 1968, **II**, **I**, 59.
8. L. Futekov und B. Atanasova, *ibid*, 1970, **III**, **I**, 65.
9. S. Wolkov, *Zavodsk. Lab.*, 1936, **5**, 1429.
10. W. Semel, *ibid.*, 1936, **5**, 1433.
11. P. Crossley, *Analyst*, 1944, **69**, 206.

Talanta, 1972, Vol. 19, pp. 821 to 824. Pergamon Press. Printed in Northern Ireland

Détermination de l'or par réaction d'échange de complexes triples à association ionique

(*Reçu le* 31 *Mars* 1971. *Accepté le* 2 *Octobre* 1971)

De nombreux anions du type $[ML_4]$, réagissant avec certains agents organiques de nature basique, fournissent des composés ordinairement peu solubles dans l'eau, mais extractibles dans des solvants organiques appropriés.

Lorsque l'agent organique—base —est un colorant, on est en présence de réactions à sensibilité élevée, mais généralement à faible sélectivité. D'autre part, les réactions de ces mêmes anions $[ML_4^-]$ avec certains agents à basicité plus prononcée, mais incolores, se distinguent par leur haute sélectivité et leur faible sensibilité.

L'usage combiné de ces deux espèces de réactions permet de créer des méthodes sensibles et en même temps suffisamment sélectives.

Le principe d'un pareil usage combiné des deux espèces de réactions peut être illustré par l'exemple suivant. L'élément à déterminer (M) est extrait sous forme de complexe $K^+[ML_x^-]$, où K^+ est un cation organique incolore. La phase organique, contenant le complexe, est traitée par une solution aqueuse, contenant un autre cation $[K_1^+]$, coloré et apte, dans des conditions données, à se substituer au premier. Le complexe coloré $K_1^+[ML_x^-]$ ainsi obtenu, passe dans la phase organique qui est ensuite soumise à la photométrie. Des données sur des réactions d'échange de chélates, ayant lieu directement dans la phase organique, existent depuis quelques années.[1-3] Dernièrement un tel échange a été utilisé pour des complexes triples, à association ionique.[4]

Dans le présent mémoire, nous avons mis à profit le principe d'echange énoncé plus haut, pour obtenir une méthode colorimétrique de détermination de l'or, sélective et sensible à la fois.

Nos essais ont prouve que l'aurichlorure de nitrone extrait avec un solvant organique peut être déterminé par voie photométrique après échange avec du bleu de méthylène.

PARTIE EXPÉRIMENTALE

Réactifs utilisés

Solution étalon d'or. Pour la préparer, on fait dissoudre 0,1000 g d'or dans quelques ml d'eau régale, et évapore la solution á sec. Le résidu est traité à trois reprises par HCl avec evaporation presque totale, puis dilué à 1000 ml avec HCl 1*M*. Avant emploi, cette solution est diluée au dixiéme par l'eau.

Solution de sulfate de nitrone—1,000 μg/ml
Solution de bleu de méthylène—0,001*M*
Solution de complexone III—0,05*M*
Chloroforme p.a.

Mode opératoire

Pendant 5 mn on extrait, par 5 ml de chloroforme, 25 ml de solution aqueuse à pH 1, contenant 3–8 μg d'or III et 1 ml de solution de sulfate de nitrone. Après séparation des phases, on transvase la couche organique dans une ampoule à décanter, on y ajoute 20 ml d'acide chlorhydrique 0,1*M*, contenant 0,4 ml de solution de bleu de méthylène, et on agite pendant 5 mn. La couche organique séparée est soumise à la centrifugation et mesurée photométriquement (filtre rouge).

DISCUSSION DES RÉSULTATS

On a étudié la formation et l'extraction de l'aurichlorure de nitrone et on les a mises à profit pour la séparation par extraction de microquantités d'or[5,6] dans des melanges complexes. Les extraits que l'on obtient contiennent ordinairement de l'or de l'ordre de 10^{-6} g/ml. En raison de cette faible teneur en or, ils sont incolores et ne peuvent être soumis directement à la photométrie. Pour cette raison et afin de pourvoir déterminer l'or, on a évaporé à sec l'extrait organique contenant l'aurichlorure de nitrone, calciné le résidu et après dissolution de l'or dans de l'eau de chlore, on l'a déterminé selon la méthode connue, à l'aide de bleu de méthylène.[7]

Dans l'extraction de l'or(III) à l'aide de nitrone, on peut extraire aussi les complexes de Tl,Pl et Pd. Les deux derniers éléments accompagnent trés rarement l'or dans les concentrés de minerai. Nos essais ont prouvé que le platine et le palladium ne gênent pas la détermination de l'or selon la méthode énoncée, les rapports respectifs étant: Au : Pt : Pd = 1 : 6 : 12.

Si, dans la détermination de l'or, on procède à la combustion du résidu (contenant de l'aurichlorure de nitrone et du thallichlorure de nitrone), le thallium ne gêne pas le dosage sous forme d'aurichlorure de bleu de méthylène. Cependant, si l'on procède par échange, le thallium interfére en donnant les résultats par excés.

Pour réaliser le dosage de l'or(III) par échange en présence de Tl(III), on a étudié les aptitudes à l'extraction de l'aurichlorure de nitrone et du thallichlorure de nitrone en fonction du pH, entre pH 1 et pH 4(Fig. 1).

Cette figure montre que l'or(III) s'extrait à l'aide de nitrone, à pH 1,82 et le thallium á pH 1,12. Pour des valeurs de pH allant de 1,12 à 1,81,l'effet gênant du Tl(III) diminue. Pour eliminer complétement son influence lors de la séparation par extraction de l'or(III) sous forme d'aurichlorure de nitrone, nous avons eu recours à la dissimulation à l'aide de complexone III et de thiocarbamide.

Dans ce but, nous avons effectué des essais en vue de déterminer séparément l'or(III) et le Tl(III) en présence de complexone III et de thiocarbamide, en modifiant leurs quantités respectives et le pH de la solution.

L'usage de complexone III nous a permis d'obtenir de tres bons resultats. Ils montrent que la concentration la plus élevée du complexone III dans la phase aqueuse, lorsque l'or(III) est extrait quantitativement, est de l'ordre de $2\cdot10^{-3}M$, le pH allant de 0,76 à 0,98. Si les valeurs de pH sont

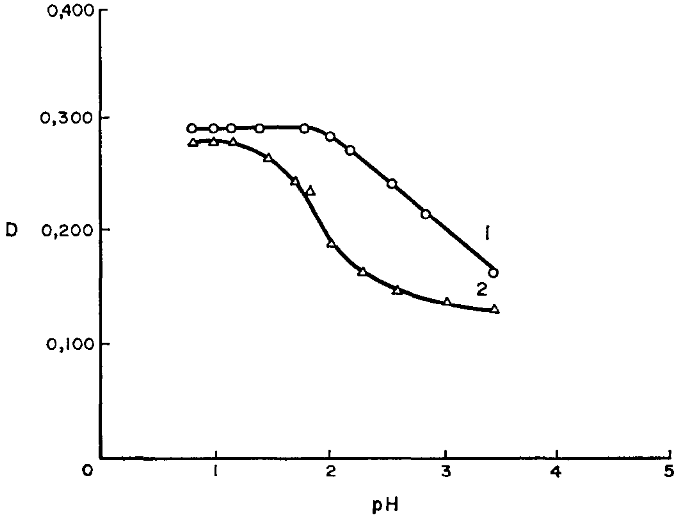


FIG. 1 —Correlation entre l'extraction de Au(III) (1) et (2) a l'aide du nitrone et en fonction du pH du milieu.

$[Au^{3+}] = [Tl^{3+}] = 50 \cdot 2$ mg/ml

supérieures à 0,98 l'extraction de l'or(III) n'est pas quantitative. On n'a pas étudié en vue de sa séparation sélective l'effet dissimulant du complexone III pour des valeurs du pH inferieures à 0,76.

Dans les conditions énoncées, Tl(III) se trouve être totalement dissimulé.

Nous avons aussi effectué des essais en vue de déterminer les quantités de Tl(III) pouvant être dissimuleés lors de la détermination d'une quantité donnée d'or (Tableau I). Ce tableau montre que, dans les conditions mentionneés, l'or(III) peut ètre déterminé par échange du nitrone dans l'aurichlorure de nitrone au moyen du bleu de méthylène en présence de 60 g Tl(III).

TABLEAU I

Prélevé		Rapport Au : Tl	Trouvé, or μg
Or, μg	Thallium, μg		
5,0	10	1 : 2	5,0
5,0	20	1 : 4	5,0
5,0	30	1 : 6	5,0
5,0	40	1 : 8	5,0
5,0	50	1 : 10	5,0
5,0	60	1 : 12	5,0
5,0	70	1 : 14	5,3

On a aussi étudié l'effet gênant des ions qui accompagnent ordinairement l'or dans les concentrés de minerai. Nos essais ont porté sur des quantités de l'ordre de 5 . 10^{-3} g des éléments cités. Il a été établi qu'ils ne peuvent pas être extraits au moyen du nitrone dans les mêmes conditions où l'on extrait l'or, et, que par conséquent, ils ne participent pas à l'échange.

Les essais effectués attestent que le principe d'echange préconisé peut être mis en pratique avec beaucoup de succèss dans la détermination photométrique de l'or en présence de thallium, de platine, de palladium et tous les autres éléments que l'accompagnent ordinairement dans les minerais et les concentrés de minerai.

Chaire de chimie analytique
Ecole normale supérieure
Rue V. Markov 7, Plovdiv, Bulgarie

N. GANTCHEV
A. DIMITROVA

Résumé—On a mis à profit le principe d'échange de complexes triples à association ionique pour déterminer l'or par photométrie. On a éthidié les effets de Pt, Pd, Tl et d'autres éléments sur la détermination de l'or(III). On a établé les conditions de détermination de l'or(III) en leur présence.

Summary—The principle of exchange of ion-association triple complexes has been used for photometric determination of gold. The effects of Pt, Pd, Tl and other elements have been examined, and conditions established for determination of gold(III) in their presence.

Zusammenfassung—Das Prinzip des Austausches von Ionenassoziations-Tripelkomplexen wurde auf die photometrische Bestimmung von Gold angewandt. Der Einfluß von Pt, Pd, Tl und anderen Elementen wurde untersucht und Bedingungen ermittelt, unter denen Gold(III) in ihrer Gegenwart bestimmt werden kann.

BIBLIOGRAPHIE

1. J. Ružička et J. Starý, *Talanta*, 1967, **14**, 909.
2. J. Starý et J. Ružička, *ibid.*, 1968, **15**, 505.
3. J. Starý, *ibid.*, 1969, **16**, 359.
4. R. W. Burke, *ibid.*, 1970, **17**, 240.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Natura*, III Fask., I, 1970.
6. N. Gantchev et A. Dimitrova, *Dokl. Acad. Sci. Bulgarie*, 1971, **24**.
7. N. Gantchev et B. Atanasova, *Zh. Analit. Khim.*, 1967, **22**, 274.

Zusammenfassung—Erhalten wurde eine neue Verbindung von Se(IV) mit Acetophenon in salzsaurem Medium, $(C_6H_5COCH_2)_4Se$. Der Prozeß der Entstehung der Verbindung dauert beim Überschuß an Acetophenon (Selen:Acetophenon < 1:4) ungefähr 300–400 Std, aber bei 60–70° nur 1,5–2 Std. Die erhaltene Verbindung löst sich sehr gut in Chloroform und Tetrachlorkohlenstoff. Diese Eigenschaft wird zur Extraktionsabtrennung von großen Mengen an Selen benutzt. Auf diese Weise wird eine gute Möglichkeit zur Bestimmung von Beimischungen in reinem Selen gegeben. Die Methode ist zur Bestimmung von Tellur in Selen angewandt worden.

Summary—A new compound has been prepared from Se(IV) and acetophenone in hydrochloric acid solution. At 60–70° conversion into $(C_6H_5COCH_2)_4Se$ is complete in 1·5–2 hr. The product is very soluble in chloroform and in carbon tetrachloride and thus offers a possibility for the separation of large quantities of selenium before determination of impurities in it. The method has been applied to the separation and determination of traces of tellurium in selenium.

Résumé—On a préparé un nouveau composé à partir de Se(IV) et d'acétophénone en solution dans l'acide chlorhydrique. A 60–70°, la conversion en $(C_6H_5COCH_2)_4Se$ est complète en 1,5–2 h. Le produit est très soluble en chloroforme et en tétrachlorure de carbone et offre ainsi une possibilité de séparation de grandes quantités de sélénium avant détermination des impuretés qu'il contient. On a appliqué la méthode à la séparation et au dosage de traces de tellurium dans le sélénium.

LITERATUR

1. N. Jordanov und L. Futekov, *Nachrichten Inst Allg. Anorg. Chemie, BAW*, 1966, **4**, 25.
2. L. Futekov und N. Jordanov, *Nachrichten Abt. Chemie, BAW*, 1968, **I**, **4**, 157.
3. N. Jordanov und L. Futekov, *Talanta*, 1965, **12**, 371.
4. *Idem*, *ibid.*, 1966, **13**, 163.
5. L. Futekov und N. Jordanov, *ibid.*, 1966, **13**, 763.
6. N. Jordanov und L. Futekov, *ibid.*, 1968, **15**, 850.
7. L. Futekov, N. Jordanov und A. Georgieva, *Natura*, 1968, **II**, **I**, 59.
8. L. Futekov und B. Atanasova, *ibid*, 1970, **III**, **I**, 65.
9. S. Wolkov, *Zavodsk. Lab.*, 1936, **5**, 1429.
10. W. Semel, *ibid.*, 1936, **5**, 1433.
11. P. Crossley, *Analyst*, 1944, **69**, 206.

Talanta, 1972, Vol. 19, pp. 821 to 824. Pergamon Press. Printed in Northern Ireland

Détermination de l'or par réaction d'échange de complexes triples à association ionique

(*Reçu le* 31 *Mars* 1971. *Accepté le* 2 *Octobre* 1971)

De nombreux anions du type [ML_4], réagissant avec certains agents organiques de nature basique, fournissent des composés ordinairement peu solubles dans l'eau, mais extractibles dans des solvants organiques appropriés.

Lorsque l'agent organique—base —est un colorant, on est en présence de réactions à sensibilité élevée, mais généralement à faible sélectivité. D'autre part, les réactions de ces mêmes anions [ML_4^-] avec certains agents à basicité plus prononcée, mais incolores, se distinguent par leur haute sélectivité et leur faible sensibilité.

L'usage combiné de ces deux espèces de réactions permet de créer des méthodes sensibles et en même temps suffisamment sélectives.

Le principe d'un pareil usage combiné des deux espèces de réactions peut être illustré par l'exemple suivant. L'élément à déterminer (M) est extrait sous forme de complexe $K^+[ML_x^-]$, où K^+ est un cation organique incolore. La phase organique, contenant le complexe, est traitée par une solution aqueuse, contenant un autre cation $[K_1^+]$, coloré et apte, dans des conditions données, à se substituer au premier. Le complexe coloré $K_1^+[ML_x^-]$ ainsi obtenu, passe dans la phase organique qui est ensuite soumise à la photométrie. Des données sur des réactions d'échange de chélates, ayant lieu directement dans la phase organique, existent depuis quelques années.[1-3] Dernièrement un tel échange a été utilisé pour des complexes triples, à association ionique.[4]

Dans le présent mémoire, nous avons mis à profit le principe d'echange énoncé plus haut, pour obtenir une méthode colorimétrique de détermination de l'or, sélective et sensible à la fois.

Nos essais ont prouve que l'aurichlorure de nitrone extrait avec un solvant organique peut être déterminé par voie photométrique après échange avec du bleu de méthylène.

PARTIE EXPÉRIMENTALE

Réactifs utilisés

Solution étalon d'or. Pour la préparer, on fait dissoudre 0,1000 g d'or dans quelques ml d'eau régale, et évapore la solution á sec. Le résidu est traité à trois reprises par HCl avec evaporation presque totale, puis dilué à 1000 ml avec HCl 1*M*. Avant emploi, cette solution est diluée au dixiéme par l'eau.

Solution de sulfate de nitrone—1,000 µg/ml
Solution de bleu de méthylène—0,001*M*
Solution de complexone III—0,05*M*
Chloroforme p.a.

Mode opératoire

Pendant 5 mn on extrait, par 5 ml de chloroforme, 25 ml de solution aqueuse à pH 1, contenant 3–8 µg d'or III et 1 ml de solution de sulfate de nitrone. Après séparation des phases, on transvase la couche organique dans une ampoule à décanter, on y ajoute 20 ml d'acide chlorhydrique 0,1*M*, contenant 0,4 ml de solution de bleu de méthylène, et on agite pendant 5 mn. La couche organique séparée est soumise à la centrifugation et mesurée photométriquement (filtre rouge).

DISCUSSION DES RÉSULTATS

On a étudié la formation et l'extraction de l'aurichlorure de nitrone et on les a mises à profit pour la séparation par extraction de microquantités d'or[5,6] dans des melanges complexes. Les extraits que l'on obtient contiennent ordinairement de l'or de l'ordre de 10^{-6} g/ml. En raison de cette faible teneur en or, ils sont incolores et ne peuvent être soumis directement à la photométrie. Pour cette raison et afin de pourvoir déterminer l'or, on a évaporé à sec l'extrait organique contenant l'aurichlorure de nitrone, calciné le résidu et après dissolution de l'or dans de l'eau de chlore, on l'a déterminé selon la méthode connue, à l'aide de bleu de méthylène.[7]

Dans l'extraction de l'or(III) à l'aide de nitrone, on peut extraire aussi les complexes de Tl,Pl et Pd. Les deux derniers éléments accompagnent trés rarement l'or dans les concentrés de minerai. Nos essais ont prouvé que le platine et le palladium ne gênent pas la détermination de l'or selon la méthode énoncée, les rapports respectifs étant: Au : Pt : Pd = 1 : 6 : 12.

Si, dans la détermination de l'or, on procède à la combustion du résidu (contenant de l'aurichlorure de nitrone et du thallichlorure de nitrone), le thallium ne gêne pas le dosage sous forme d'aurichlorure de bleu de méthylène. Cependant, si l'on procède par échange, le thallium interfére en donnant les résultats par excés.

Pour réaliser le dosage de l'or(III) par échange en présence de Tl(III), on a étudié les aptitudes à l'extraction de l'aurichlorure de nitrone et du thallichlorure de nitrone en fonction du pH, entre pH 1 et pH 4(Fig. 1).

Cette figure montre que l'or(III) s'extrait à l'aide de nitrone, à pH 1,82 et le thallium á pH 1,12. Pour des valeurs de pH allant de 1,12 à 1,81,l'effet gênant du Tl(III) diminue. Pour eliminer complétement son influence lors de la séparation par extraction de l'or(III) sous forme d'aurichlorure de nitrone, nous avons eu recours à la dissimulation à l'aide de complexone III et de thiocarbamide.

Dans ce but, nous avons effectué des essais en vue de déterminer séparément l'or(III) et le Tl(III) en présence de complexone III et de thiocarbamide, en modifiant leurs quantités respectives et le pH de la solution.

L'usage de complexone III nous a permis d'obtenir de tres bons resultats. Ils montrent que la concentration la plus élevée du complexone III dans la phase aqueuse, lorsque l'or(III) est extrait quantitativement, est de l'ordre de $2\cdot10^{-3}M$, le pH allant de 0,76 à 0,98. Si les valeurs de pH sont

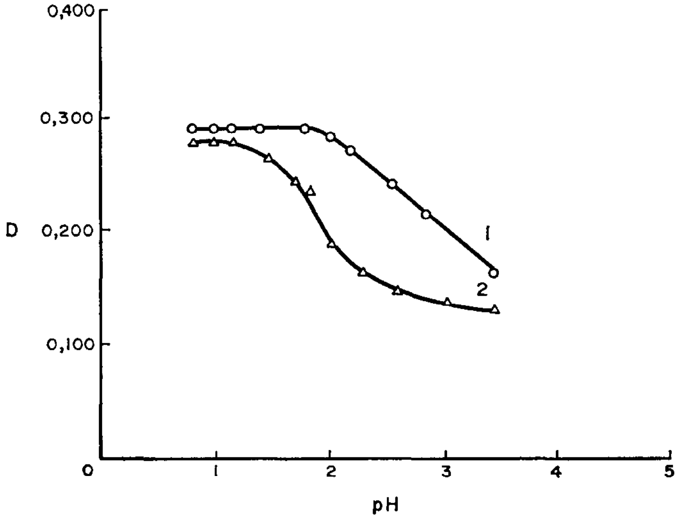


FIG. 1 —Correlation entre l'extraction de Au(III) (1) et (2) a l'aide du nitrone et en fonction du pH du milieu.

$[Au^{3+}] = [Tl^{3+}] = 50{\cdot}2$ mg/ml

supérieures à 0,98 l'extraction de l'or(III) n'est pas quantitative. On n'a pas étudié en vue de sa séparation sélective l'effet dissimulant du complexone III pour des valeurs du pH inferieures à 0,76.

Dans les conditions énoncées, Tl(III) se trouve être totalement dissimulé.

Nous avons aussi effectué des essais en vue de déterminer les quantités de Tl(III) pouvant être dissimuleés lors de la détermination d'une quantité donnée d'or (Tableau I). Ce tableau montre que, dans les conditions mentionneés, l'or(III) peut ètre déterminé par échange du nitrone dans l'aurichlorure de nitrone au moyen du bleu de méthylène en présence de 60 g Tl(III).

TABLEAU I

Prélevé		Rapport Au : Tl	Trouvé, or µg
Or, µg	Thallium, µg		
5,0	10	1 : 2	5,0
5,0	20	1 : 4	5,0
5,0	30	1 : 6	5,0
5,0	40	1 : 8	5,0
5,0	50	1 : 10	5,0
5,0	60	1 : 12	5,0
5,0	70	1 : 14	5,3

On a aussi étudié l'effet gênant des ions qui accompagnent ordinairement l'or dans les concentrés de minerai. Nos essais ont porté sur des quantités de l'ordre de $5 \,.\, 10^{-3}$ g des éléments cités. Il a été établi qu'ils ne peuvent pas être extraits au moyen du nitrone dans les mêmes conditions où l'on extrait l'or, et, que par conséquent, ils ne participent pas à l'échange.

Les essais effectués attestent que le principe d'echange préconisé peut être mis en pratique avec beaucoup de succèss dans la détermination photométrique de l'or en présence de thallium, de platine, de palladium et tous les autres éléments que l'accompagnent ordinairement dans les minerais et les concentrés de minerai.

Chaire de chimie analytique
Ecole normale supérieure
Rue V. Markov 7, Plovdiv, Bulgarie

N. GANTCHEV
A. DIMITROVA

Résumé—On a mis à profit le principe d'échange de complexes triples à association ionique pour déterminer l'or par photométrie. On a éthidié les effets de Pt, Pd, Tl et d'autres éléments sur la détermination de l'or(III). On a établé les conditions de détermination de l'or(III) en leur présence.

Summary—The principle of exchange of ion-association triple complexes has been used for photometric determination of gold. The effects of Pt, Pd, Tl and other elements have been examined, and conditions established for determination of gold(III) in their presence.

Zusammenfassung—Das Prinzip des Austausches von Ionenassoziations-Tripelkomplexen wurde auf die photometrische Bestimmung von Gold angewandt. Der Einfluß von Pt, Pd, Tl und anderen Elementen wurde untersucht und Bedingungen ermittelt, unter denen Gold(III) in ihrer Gegenwart bestimmt werden kann.

BIBLIOGRAPHIE

1. J. Ružička et J. Starý, *Talanta*, 1967, **14**, 909.
2. J. Starý et J. Ružička, *ibid.*, 1968, **15**, 505.
3. J. Starý, *ibid.*, 1969, **16**, 359.
4. R. W. Burke, *ibid.*, 1970, **17**, 240.
5. N. Gantchev, A. Dimitrova et L. Futekov, *Natura*, III Fask., I, 1970.
6. N. Gantchev et A. Dimitrova, *Dokl. Acad. Sci. Bulgarie*, 1971, **24**.
7. N. Gantchev et B. Atanasova, *Zh. Analit. Khim.*, 1967, **22**, 274.

Talanta, 1972, Vol. 19, pp. 825 to 827. Pergamon Press. Printed in Northern Ireland

PRELIMINARY COMMUNICATIONS

Extraction of some metal phenylacetates into chloroform

(*Received* 4 *October* 1971. *Accepted* 25 *November* 1971)

During the investigation of new compounds for highly selective extraction of metals we have paid attention to phenylacetic acid—$C_6H_5CH_2COOH$ (PAA). An aqueous solution of this acid will precipitate iron(III), copper(II), uranyl ion *etc* from slightly acidic or nearly neutral solutions (pH 6). The precipitate dissolves easily in chloroform and other organic solvents.

With further experimentation we have found that phenylacetic acid offers more selective reactions than does, for example, oxine. From slightly acidic dilute solutions large amounts of nickel, cobalt, manganese, alkaline earth metals, molybdate, vanadate are not precipitated or extracted. The extraction capacity for iron, copper and uranium is very large, exceeding the extractibility of most other metal chelates. It is possible to extract smoothly 200 mg and more of iron in the presence of micro amounts of nickel, cobalt or manganese.

There are some possibilities for using such separations on the micro-scale for colorimetric determination of particular elements as well on the macro-scale for complexometric determinations. Phenylacetic acid is slightly soluble in water (1·26 g/100 ml) but very soluble in chloroform. Its chloroform solution was therefore used as extractant. We can expect that other substituted acetic acids will behave similarly. Extractable precipitates are formed, for example, by 1-hydroxynaphthylacetic acid.

In this work the dependence of the extraction on pH and metal ion concentration was studied, because it has been observed that the extractability of individual metals varies very much.

EXPERIMENTAL

Reagents

*Phenylacetic acid solution, 1*M *in chloroform.* Prepared by dissolution of 34·0 g of PAA in 250 ml of chloroform.

*Metal solutions, 0·05*M. Prepared from the salts (sulphate, chloride, nitrate) and checked complexometrically.

*EDTA solution 0·05*M. Standardized with 0·05*M* lead nitrate, with Xylenol Orange as indicator.

Other reagents include saturated solutions of hexamethylenetetramine (hexamine), borax and ammonium acetate.

Influence of pH on the extraction

Because the extraction of the metals is primarily dependent on quantitative precipitation, it was obvious that the solution before extraction should not be acid. Tervalent iron is only partly extracted at pH 3–4 but quantitatively at pH 6. The same holds for other elements. Iron gives an orange to deep red extract, copper gives an intense blue from borax medium or a green extract from hexamine solutions. Easily hydrolysed metals—zirconium, hafnium, thorium, bismuth, aluminium, titanium—are not extracted, forming precipitates at the chloroform interface which are partly suspended in the chloroform.

The first experiments were carried out as follows. To the acidic metal solution solid PAA was added and the solution was extracted with chloroform. Usually all the PAA was dissolved. Then the pH was adjusted to about 6 by addition of saturated solutions of hexamine, borax or ammonium acetate, and the solution was shaken again. In later experiments a 1*M* solution of PAA in chloroform was used.

Effect of dilution on the extraction

As already said, the extraction can be carried out only after precipitation of particular metals. Some metal phenylacetates are soluble and precipitate only from relatively concentrated solutions. The results in Table I for bivalent metals, iron(III) and uranyl ion were obtained by the following procedure. To 2 ml of 0·05*M* metal solution in a 150-ml separatory funnel, water was added (0, 5, 10 ml) followed by 5 ml of buffer solution. The mixture was extracted for 1 min with 5 ml of 1*M*

TABLE I.—DEGREE OF EXTRACTION (%) OF METAL PHENYLACETATES
(For 2 ml of 0·05*M* metal solutions)

Final volume, *ml*	7	12	17	7	7
Buffer	Hexamine (a)	Hexamine (a)	Hexamine (a)	Borax (b)	$NH_4O_2C{\cdot}CH_3$ (c)
Final molarity of the metal solution	$1{\cdot}4 \times 10^{-2}$	$8{\cdot}3 \times 10^{-3}$	$5{\cdot}8 \times 10^{-3}$	$1{\cdot}4 \times 10^{-2}$	
Co(II)	60	25	13	5	1
Ni	49	18	8	0	0
Pb	100	100	100	85	0
Zn	98	96	90	0	0·9
Cd	91	83	30	0	0
Mn(II)	0	0	0	0	0
Cu(II)	99	99	99	99	20
Fe(III)	100	100	100	100	100
UO_2^{2+}	100	100	100	100	98

(*a*) pH 5–5·5 (*b*) pH 6 (*c*) pH 4–6 in final solutions.

PAA in chloroform. The phases were separated and the aqueous phase was extracted once more with 5 ml of pure chloroform. The metal left in the aqueous phase after dilution with water was determined by a suitable complexometric method. The degree of extraction is summarized in Table I.

From Table I we can see that in the case of bivalent metals, with the exception of copper, the degree of extraction is very dependent on the metal concentration. It can be expected that at high dilution (about 0·01*M*) these metals are not extracted at all. The second series of extractions of bivalent metals and some others was carried out as follows. A 5-ml portion of 0·05*M* metal solution in a 150–250-ml separatory funnel was diluted to 50, 100 or 150 ml. After addition of 20 ml of saturated hexamine solution and 10 ml of 1*M* PAA in chloroform, the mixture was shaken for 1 min. After separation of the phases, the aqueous phase was extracted twice with 10-ml portions of pure chloroform. The metal remaining in the aqueous phase was determined complexometrically. The consumption of 0·05 ml or less of 0·05*M* EDTA in the titration of the aqueous phase was considered as zero for the calculation of the degree of extraction. Some results are summarized in Table II.

TABLE II.—DEGREE OF EXTRACTION (%) OF METAL PHENYLACETATES FROM LARGE VOLUMES
(For 5 ml of 0·05*M* metal solutions; hexamine buffer pH 5·5–6)

Final volume, *ml*	70	120	170
Final molarity of metal before extraction	$3{\cdot}5 \times 10^{-3}$	2×10^{-3}	$1{\cdot}47 \times 10^{-3}$
Co(II)	0	0	0
Ni	0	0	0
Pb	88	56	28
Zn	0	0	0
Cd	0	0	0
Mn(II)	0	0	0
Cu(II)	100	100	100
In	100	100	100
Ga	100	100	100
La	68	16	0
Ce(IV)	100	99	94
Ce(III)	36	1	0
Pr	96	74	0
Dy	75	50	3
Y	56	4	1
Sc	92	92	100

The extraction of some metals by the described procedure was followed only qualitatively. These observations are given in Table III.

TABLE III.—EXTRACTION OF LESS COMMON METALS
(qualitative tests)

Metal ion	Extraction	Aqueous phase
Vanadium(IV)	Violet extract	Negative test with H_2O_2
Vanadium(V)	Not extracted	Intense yellow
Molybdenum(VI)	Not extracted	Oxine precipitation
Tungsten(VI)	Not extracted	Oxine precipitation
Gold(III)	Yellow extract	Colourless
Platinum(IV)	Yellow extract	Colourless
Palladium(II)	Yellow-brown	Colourless
Germanium(IV)	Not extracted	Positive test with phenylfluorone

Influence of masking

Complex-forming compounds will compete with the formation of the phenylacetate precipitate. For example, copper is extracted incompletely in the presence of ammonium acetate, and lead not at all (see Table I). EDTA prevents all precipitations. Ammonium fluoride masks iron and uranium, making extraction of copper highly selective. On the other hand copper can be masked with thiourea, uranium with hydrogen peroxide or ammonium carbonate *etc.*

Table II offers some possibilities for the separation of metals. From the practical point of view this type of extraction is suitable for removal of larger amounts of iron, copper and uranium from complex material. Further experiments have shown that it is possible to determine minute traces of manganese in iron or steels (with formaldoxime) or cobalt (less than 0·05%) in the same material with nitroso-R-salt, or to determine complexometrically zinc and manganese in copper alloys, nickel or cobalt in various iron alloys *etc.* The results will be published elsewhere.

Analytical Laboratory
Institute of Geological Sciences
Charles University, Prague 2
Albertov 6

JIŘÍ ADAM

Analytical Laboratory
J. Heyrovský Polarographic Institute
Czechoslovak Academy of Science
Prague 1, *Jilská* 16
Czechoslovakia

RUDOLF PŘIBIL
VLADIMÍR VESELÝ

Summary—Phenylacetic acid has been found to be very useful as a reagent in the extraction of large quantities of certain ions, notable iron(III), cobalt(II), copper(II), lead, zinc, cadmium and uranyl. A 1*M* solution of the reagent in chloroform is used to extract up to 200 mg of certain ions from small volumes of aqueous phase. Selectivity is increased by pH control and masking.

Zusammenfassung—Phenylessigsäure ist sehr nützlich als Reagens zur Extraktion großer Mengen bestimmter Ionen, besonders Eisen(III), Kobalt(II), Kupfer(II), Blei, Zink, Cadmium und Uranyl. Eine 1*M* Lösung des Reagens in Chloroform dient zur Extraktion von bis zu 200 mg dieser Ionen aus kleinen Volumina wäßriger Phase. Die Selektivität wird durch pH-Kontrolle und Maskierung verbessert.

Résumé—On a trouvé que l'acide phénylacétique est très utile en tant que réactif pour l'extraction de grandes quantités de certains ions, notamment les fer(III), cobalt(II), cuivre(II), plomb, zinc, cadium et uranyle. On utilise une solution 1*M* du réactif en chloroforme pour extraire jusqu'à 200 mg de certains ions de petits volumes de phase aqueuse. La sélectivité est accrue par contrôle de pH et dissimulation.

Talanta, 1972, Vol. 19, pp. 825 to 827. Pergamon Press. Printed in Northern Ireland

PRELIMINARY COMMUNICATIONS

Extraction of some metal phenylacetates into chloroform

(*Received* 4 *October* 1971. *Accepted* 25 *November* 1971)

DURING the investigation of new compounds for highly selective extraction of metals we have paid attention to phenylacetic acid—$C_6H_5CH_2COOH$ (PAA). An aqueous solution of this acid will precipitate iron(III), copper(II), uranyl ion *etc* from slightly acidic or nearly neutral solutions (pH 6). The precipitate dissolves easily in chloroform and other organic solvents.

With further experimentation we have found that phenylacetic acid offers more selective reactions than does, for example, oxine. From slightly acidic dilute solutions large amounts of nickel, cobalt, manganese, alkaline earth metals, molybdate, vanadate are not precipitated or extracted. The extraction capacity for iron, copper and uranium is very large, exceeding the extractibility of most other metal chelates. It is possible to extract smoothly 200 mg and more of iron in the presence of micro amounts of nickel, cobalt or manganese.

There are some possibilities for using such separations on the micro-scale for colorimetric determination of particular elements as well on the macro-scale for complexometric determinations. Phenylacetic acid is slightly soluble in water (1·26 g/100 ml) but very soluble in chloroform. Its chloroform solution was therefore used as extractant. We can expect that other substituted acetic acids will behave similarly. Extractable precipitates are formed, for example, by 1-hydroxynaphthylacetic acid.

In this work the dependence of the extraction on pH and metal ion concentration was studied, because it has been observed that the extractability of individual metals varies very much.

EXPERIMENTAL

Reagents

*Phenylacetic acid solution, 1*M *in chloroform.* Prepared by dissolution of 34·0 g of PAA in 250 ml of chloroform.

*Metal solutions, 0·05*M. Prepared from the salts (sulphate, chloride, nitrate) and checked complexometrically.

*EDTA solution 0·05*M. Standardized with 0·05*M* lead nitrate, with Xylenol Orange as indicator.

Other reagents include saturated solutions of hexamethylenetetramine (hexamine), borax and ammonium acetate.

Influence of pH on the extraction

Because the extraction of the metals is primarily dependent on quantitative precipitation, it was obvious that the solution before extraction should not be acid. Tervalent iron is only partly extracted at pH 3–4 but quantitatively at pH 6. The same holds for other elements. Iron gives an orange to deep red extract, copper gives an intense blue from borax medium or a green extract from hexamine solutions. Easily hydrolysed metals—zirconium, hafnium, thorium, bismuth, aluminium, titanium—are not extracted, forming precipitates at the chloroform interface which are partly suspended in the chloroform.

The first experiments were carried out as follows. To the acidic metal solution solid PAA was added and the solution was extracted with chloroform. Usually all the PAA was dissolved. Then the pH was adjusted to about 6 by addition of saturated solutions of hexamine, borax or ammonium acetate, and the solution was shaken again. In later experiments a 1*M* solution of PAA in chloroform was used.

Effect of dilution on the extraction

As already said, the extraction can be carried out only after precipitation of particular metals. Some metal phenylacetates are soluble and precipitate only from relatively concentrated solutions. The results in Table I for bivalent metals, iron(III) and uranyl ion were obtained by the following procedure. To 2 ml of 0·05*M* metal solution in a 150-ml separatory funnel, water was added (0, 5, 10 ml) followed by 5 ml of buffer solution. The mixture was extracted for 1 min with 5 ml of 1*M*

TABLE I.—DEGREE OF EXTRACTION (%) OF METAL PHENYLACETATES
(For 2 ml of 0·05*M* metal solutions)

Final volume, *ml*	7	12	17	7	7
Buffer	Hexamine (a)	Hexamine (a)	Hexamine (a)	Borax (b)	$NH_4O_2C{\cdot}CH_3$ (c)
Final molarity of the metal solution	$1{\cdot}4 \times 10^{-2}$	$8{\cdot}3 \times 10^{-3}$	$5{\cdot}8 \times 10^{-3}$	$1{\cdot}4 \times 10^{-2}$	
Co(II)	60	25	13	5	1
Ni	49	18	8	0	0
Pb	100	100	100	85	0
Zn	98	96	90	0	0·9
Cd	91	83	30	0	0
Mn(II)	0	0	0	0	0
Cu(II)	99	99	99	99	20
Fe(III)	100	100	100	100	100
UO_2^{2+}	100	100	100	100	98

(*a*) pH 5–5·5 (*b*) pH 6 (*c*) pH 4–6 in final solutions.

PAA in chloroform. The phases were separated and the aqueous phase was extracted once more with 5 ml of pure chloroform. The metal left in the aqueous phase after dilution with water was determined by a suitable complexometric method. The degree of extraction is summarized in Table I.

From Table I we can see that in the case of bivalent metals, with the exception of copper, the degree of extraction is very dependent on the metal concentration. It can be expected that at high dilution (about 0·01*M*) these metals are not extracted at all. The second series of extractions of bivalent metals and some others was carried out as follows. A 5-ml portion of 0·05*M* metal solution in a 150–250-ml separatory funnel was diluted to 50, 100 or 150 ml. After addition of 20 ml of saturated hexamine solution and 10 ml of 1*M* PAA in chloroform, the mixture was shaken for 1 min. After separation of the phases, the aqueous phase was extracted twice with 10-ml portions of pure chloroform. The metal remaining in the aqueous phase was determined complexometrically. The consumption of 0·05 ml or less of 0·05*M* EDTA in the titration of the aqueous phase was considered as zero for the calculation of the degree of extraction. Some results are summarized in Table II.

TABLE II.—DEGREE OF EXTRACTION (%) OF METAL PHENYLACETATES FROM LARGE VOLUMES
(For 5 ml of 0·05*M* metal solutions; hexamine buffer pH 5·5–6)

Final volume, *ml*	70	120	170
Final molarity of metal before extraction	$3{\cdot}5 \times 10^{-3}$	2×10^{-3}	$1{\cdot}47 \times 10^{-3}$
Co(II)	0	0	0
Ni	0	0	0
Pb	88	56	28
Zn	0	0	0
Cd	0	0	0
Mn(II)	0	0	0
Cu(II)	100	100	100
In	100	100	100
Ga	100	100	100
La	68	16	0
Ce(IV)	100	99	94
Ce(III)	36	1	0
Pr	96	74	0
Dy	75	50	3
Y	56	4	1
Sc	92	92	100

The extraction of some metals by the described procedure was followed only qualitatively. These observations are given in Table III.

TABLE III.—EXTRACTION OF LESS COMMON METALS
(qualitative tests)

Metal ion	Extraction	Aqueous phase
Vanadium(IV)	Violet extract	Negative test with H_2O_2
Vanadium(V)	Not extracted	Intense yellow
Molybdenum(VI)	Not extracted	Oxine precipitation
Tungsten(VI)	Not extracted	Oxine precipitation
Gold(III)	Yellow extract	Colourless
Platinum(IV)	Yellow extract	Colourless
Palladium(II)	Yellow-brown	Colourless
Germanium(IV)	Not extracted	Positive test with phenylfluorone

Influence of masking

Complex-forming compounds will compete with the formation of the phenylacetate precipitate. For example, copper is extracted incompletely in the presence of ammonium acetate, and lead not at all (see Table I). EDTA prevents all precipitations. Ammonium fluoride masks iron and uranium, making extraction of copper highly selective. On the other hand copper can be masked with thiourea, uranium with hydrogen peroxide or ammonium carbonate *etc.*

Table II offers some possibilities for the separation of metals. From the practical point of view this type of extraction is suitable for removal of larger amounts of iron, copper and uranium from complex material. Further experiments have shown that it is possible to determine minute traces of manganese in iron or steels (with formaldoxime) or cobalt (less than 0·05%) in the same material with nitroso-R-salt, or to determine complexometrically zinc and manganese in copper alloys, nickel or cobalt in various iron alloys *etc.* The results will be published elsewhere.

Analytical Laboratory
Institute of Geological Sciences
Charles University, Prague 2
Albertov 6

JIŘÍ ADAM

Analytical Laboratory
J. Heyrovský Polarographic Institute
Czechoslovak Academy of Science
Prague 1, *Jilská* 16
Czechoslovakia

RUDOLF PŘIBIL
VLADIMÍR VESELÝ

Summary—Phenylacetic acid has been found to be very useful as a reagent in the extraction of large quantities of certain ions, notable iron(III), cobalt(II), copper(II), lead, zinc, cadmium and uranyl. A 1*M* solution of the reagent in chloroform is used to extract up to 200 mg of certain ions from small volumes of aqueous phase. Selectivity is increased by pH control and masking.

Zusammenfassung—Phenylessigsäure ist sehr nützlich als Reagens zur Extraktion großer Mengen bestimmter Ionen, besonders Eisen(III), Kobalt(II), Kupfer(II), Blei, Zink, Cadmium und Uranyl. Eine 1*M* Lösung des Reagens in Chloroform dient zur Extraktion von bis zu 200 mg dieser Ionen aus kleinen Volumina wäßriger Phase. Die Selektivität wird durch pH-Kontrolle und Maskierung verbessert.

Résumé—On a trouvé que l'acide phénylacétique est très utile en tant que réactif pour l'extraction de grandes quantités de certains ions, notamment les fer(III), cobalt(II), cuivre(II), plomb, zinc, cadium et uranyle. On utilise une solution 1*M* du réactif en chloroforme pour extraire jusqu'à 200 mg de certains ions de petits volumes de phase aqueuse. La sélectivité est accrue par contrôle de pH et dissimulation.

Talanta, 1972, Vol. 19, pp. 828 to 830. Pergamon Press. Printed in Northern Ireland

Foam chromatography

Solid foams as supports in column chromatography

(*Received* 25 *October* 1971. *Accepted* 4 *December* 1971)

THIS PRELIMINARY NOTE deals with a new possibility in reversed-phase partition (extraction) chromatography. The concept may also be extended to ion-exchange and analogous techniques. Our investigations in these fields are in progress. In the last decades extraction chromatography has undergone considerable progress[1-4] and numerous separations have become possible which could only be achieved with difficulty, or not at all, by static extraction. General use of this method was limited by two major problems: the lack of inert supports with suitable chemical and physical properties, and the relatively low capacity of the extraction chromatographic columns.

A solution of the first problem has been given by the application of organic polymeric (plastic) inert supports. Thus the introduction, for use in column chromatography, of polytrifluoroethylene (Kel-F),[5-7] polytetrafluoroethylene (Teflon, Haloport-F, Fluoroplast),[8,9] the copolymer of polyvinyl acetate and polyvinyl chloride (Corvic),[10] the copolymer of styrene and divinylbenzene,[11] polyethylene (Mipor)[12] and polyfluorocarbon[13] represents marked progress. These supports are applied in granular form, and the adsorption and elution of the components to be separated take place in a thin film of the stationary phase coated on the polymer surface. The considerable advantages of the application of such plastic supports are lessened by the necessity of using them as finely granulated particles, with large specific surface, in order to increase the capacity; this adversely affects the flow-rate through the column, and therefore pressurized columns have to be employed. Even in this case, the capacity is less than that of ion-exchange resins.

For a solution of the problems mentioned above, the idea occurred that chromatographic adsorption, exchange and partition processes could be favourably influenced by giving the adsorbent a hollow spherical (cellular) form, and effecting the adsorption on the internal surface of the cells. This can be done by using solid, flexible, foamed synthetic polymers as inert supports in columns. Open-cell plastic foams may be regarded as a relatively regular stack of hollow spheres (cells).

The hydrodynamic properties of chromatographic columns packed with a foamed polymer are extremely favourable, and high flow-rates may be attained. The large specific surface of the foams ensures a large capacity compared with granular supports. In ion-exchange chromatography it may also be expected that the rate of the exchange processes will increase when the thin membranes forming the inner surface of the cells provide the site of exchange.

With the highly developed technology for making foamed plastics and synthetic polymers today,[14] probably many or all organic supports, applied hitherto in granular form, may be produced as a foam.

To our knowledge, results have not been published so far on the application of plastic foams as supports in chromatographic columns, though Bowen[15] recently suggested polyurethane foams as adsorbents in batch adsorption separations.

Our investigations were initiated with plastic foams available on the market. The first experiments concerned mainly the flow characteristics and chemical resistance of the foams applied.

Of the different foams examined (PVC, viscose, rubber and polyurethane), polyurethane foam proved to be the most appropriate, hence only this was subjected to a more thorough examination. Attempts at the preparation of other foamed inert synthetic and ion-exchange polymers are in progress.

As a model, the extraction chromatographic separation of palladium, in the form of palladium-thiourea complex in perchloric acid medium, was examined, with tri-n-butyl phosphate[16] on polyurethane foam as the stationary phase.

EXPERIMENTAL

Reagents and material

All reagents used were of analytical grade unless otherwise mentioned. Tri-n-butyl phosphate (TBP) used as the stationary phase was purified according to the procedure described by Hamlin *et al.*[7] Polyurethane foam, polyether of open cell-type, was used as the supporting material. It was a flexible polymer with 60 cells/cm on the average. This material was supplied by the North Hungarian Chemical Works, Sajóbábony, Hungary.

Column packing

A column of 1·5 cm bore and 15 cm length (with inlet and outlet taps at both ends) was used. The polyurethane packing material was washed 3 times with acetone. The dried material either in the form of small cubes or cylinders was equilibrated with purified TBP (3 ml per g of foam) with efficient stirring, then left overnight. The loaded foam was dried between two sheets of filter paper to remove excess of TBP. The cylindrical foam was cut such that each rod had a little larger diameter than that of the column. Either form of the loaded foam was evenly packed in the column by gentle pressure with a glass rod. This procedure reduced the volume of the compressed foam to one third of its original value. The packed column was evacuated by means of an oil-pump. Distilled water saturated with TBP was gradually allowed to fill the column through the outlet tap. This allows any residual air bubbles to escape from the foam inner surface to the top of the column and results in a homogeneous bed.

Procedure

Separation of Pd *and* Ni. The feed solution contained 1 ml of $PdCl_2$ solution (Pd 1 mg/ml), 1 ml of $NiCl_2$ solution (Ni 1 mg/ml) and 10 ml of 0·1*M* perchloric acid containing 3% thiourea and 1% sodium perchlorate. Different experiments were made in which the concentration of Pd was kept constant while that of Ni was varied by a factor of up to 100.

Sorption of this mixture took place at a flow-rate of 1 ml/min. The mixture was chromatographed at flow-rates of 1–4 ml/min.

Water saturated with TBP was used as eluting solution. Ni was eluted with 0·1*M* perchloric acid containing 3% thiourea and 1% sodium perchlorate, and Pd with water. In both cases the eluent was saturated with TBP, which served to keep the concentration of TBP on the foam material constant. Pd and Ni were determined spectrophotometrically as the Pd–thiourea and Ni–dimethylglyoxime complexes, at 292 and 366 nm respectively.

RESULTS AND DISCUSSION

Under the experimental conditions used Ni does not form a complex with thiourea,[17] and comes off the column in the first free column volumes without any measurable retention. On the other hand, Pd, which forms a complex with thiourea, was completely taken up by the loaded foam even in presence of 100 times its weight of Ni.

In comparison with published work[18] in which TBP was used as stationary phase loaded on different inert supports in granular form, it was found that polyurethane foam column support takes up TBP much more efficiently. For example, Kel-F takes up 1 ml of TBP per g, whereas polyurethane foam takes up 2 ml/g. This high uptake of stationary phase results in a high relative break-through capacity of the column, *i.e.*, ~30 mg of Pd^{2+} per g of coated foam.

Sharp and symmetrical peaks were obtained for both Ni and Pd. For Pd the height equivalent to one theoretical plate (HETP) was calculated to be ~1·4 mm.

The flow-rates were considerably higher than for granular supports,[15,18] without pressure applied at the top of the columns.

Institute of Inorganic and Analytical Chemistry,
L. Eötrös University, Budapest 8,
Muzeum krt. 4/6, Hungary.

T. BRAUN
A. B. FARAG

Summary—Foamed polymer is loaded with tributyl phosphate as stationary phase and compressed into a chromatographic column which will give flow rates of 1–4 ml/min, has a high break-through capacity and gives sharp and symmetrical peaks in elution chromatography. It has been applied to separation of nickel and palladium.

Zusammenfassung—Ein Polymerenschaum wird mit Tributylphosphat als stationärer Phase getränkt und in eine Chromatographiesäule gepreßt. Man erreicht Durchflußgeschwindigkeiten von 1–4 ml/min, eine hohe Durchbruchskapazität und bei der Elutionschromatographie scharfe und symmetrische Peaks. Das Verfahren wurde auf die Trennung von Nickel und Palladium angewandt.

Résumé—Un polymère-mousse chargé de phosphate de tributyle comme phase stationnaire et comprimé dans une colonne chromatographique qui donnera des vitesses d'écoulement de 1–4 ml/mn donne des pics accentués et symétriques en chromatographie d'élution. On l'a appliqué à la séparation du nickel et du palladium.

REFERENCES

1. I. Stronski, *Öster. Chem. Ztg.*, 1967, **68**, 5.
2. V. Speváčkova, *Chem. Listy*, 1968, **62**, 1194.
3. G. S. Katykhin, *Zh. Analit. Khim.*, 1965, **20**, 615.
4. C. Poitrenaud, *Chim. Anal.*, 1970, **52**, 39.
5. E. Cerrai and C. Testa, *J. Chromatog.*, 1962, **9**, 216.
6. W. Fletcher, *U.S. At. Energy. Comm. Rept.*, TID-7629, 276 (1961).
7. A. G. Hamlin, B. J. Roberts, W. Loughlin and S. G. Walker, *Anal. Chem.*, 1961, **33**, 1547.
8. J. S. Fritz and C. E. Hedrick, *Anal. Chem.*, 1962, **34**, 1411.
9. A. V. Kaljamin, *Radiokhimiya*, 1963, **5**, 749.
10. T. B. Pierce and P. F. Peck, *Nature*, 1962, **194**, 84.
11. H. Small, *J. Inorg. Nucl. Chem.*, 1961, **18**, 232.
12. V. A. Winsten, *Anal. Chem.*, 1962, **34**, 1334.
13. F. Nelson, *J. Chromatog.*, 1966, **20**, 378.
14. F. H. Ferrigno, *Rigid Plastics Foams*, Reinhold, New York, 1963.
15. H. J. M. Bowen, *J. Chem. Soc. A*, 1970, 1082.
16. M. Yusaf, Z. Sulcek and J. Doležal, *Anal. Lett.*, 1971, **4**, 119.
17. K. Swaminathan and H. M. N. H. Irving, *J. Inorg. Nucl. Chem.*, 1966, **28**, 171.
18. I. Akaza, T. Kiba and M. Taba, *Bull. Chem. Soc. Japan*, 1969, **42**, 1291.

Talanta, 1972, Vol. 19, pp. 828 to 830. Pergamon Press. Printed in Northern Ireland

Foam chromatography

Solid foams as supports in column chromatography

(*Received* 25 *October* 1971. *Accepted* 4 *December* 1971)

THIS PRELIMINARY NOTE deals with a new possibility in reversed-phase partition (extraction) chromatography. The concept may also be extended to ion-exchange and analogous techniques. Our investigations in these fields are in progress. In the last decades extraction chromatography has undergone considerable progress[1-4] and numerous separations have become possible which could only be achieved with difficulty, or not at all, by static extraction. General use of this method was limited by two major problems: the lack of inert supports with suitable chemical and physical properties, and the relatively low capacity of the extraction chromatographic columns.

A solution of the first problem has been given by the application of organic polymeric (plastic) inert supports. Thus the introduction, for use in column chromatography, of polytrifluoroethylene (Kel-F),[5-7] polytetrafluoroethylene (Teflon, Haloport-F, Fluoroplast),[8,9] the copolymer of polyvinyl acetate and polyvinyl chloride (Corvic),[10] the copolymer of styrene and divinylbenzene,[11] polyethylene (Mipor)[12] and polyfluorocarbon[13] represents marked progress. These supports are applied in granular form, and the adsorption and elution of the components to be separated take place in a thin film of the stationary phase coated on the polymer surface. The considerable advantages of the application of such plastic supports are lessened by the necessity of using them as finely granulated particles, with large specific surface, in order to increase the capacity; this adversely affects the flow-rate through the column, and therefore pressurized columns have to be employed. Even in this case, the capacity is less than that of ion-exchange resins.

For a solution of the problems mentioned above, the idea occurred that chromatographic adsorption, exchange and partition processes could be favourably influenced by giving the adsorbent a hollow spherical (cellular) form, and effecting the adsorption on the internal surface of the cells. This can be done by using solid, flexible, foamed synthetic polymers as inert supports in columns. Open-cell plastic foams may be regarded as a relatively regular stack of hollow spheres (cells).

The hydrodynamic properties of chromatographic columns packed with a foamed polymer are extremely favourable, and high flow-rates may be attained. The large specific surface of the foams ensures a large capacity compared with granular supports. In ion-exchange chromatography it may also be expected that the rate of the exchange processes will increase when the thin membranes forming the inner surface of the cells provide the site of exchange.

With the highly developed technology for making foamed plastics and synthetic polymers today,[14] probably many or all organic supports, applied hitherto in granular form, may be produced as a foam.

To our knowledge, results have not been published so far on the application of plastic foams as supports in chromatographic columns, though Bowen[15] recently suggested polyurethane foams as adsorbents in batch adsorption separations.

Our investigations were initiated with plastic foams available on the market. The first experiments concerned mainly the flow characteristics and chemical resistance of the foams applied.

Of the different foams examined (PVC, viscose, rubber and polyurethane), polyurethane foam proved to be the most appropriate, hence only this was subjected to a more thorough examination. Attempts at the preparation of other foamed inert synthetic and ion-exchange polymers are in progress.

As a model, the extraction chromatographic separation of palladium, in the form of palladium–thiourea complex in perchloric acid medium, was examined, with tri-n-butyl phosphate[16] on polyurethane foam as the stationary phase.

EXPERIMENTAL

Reagents and material

All reagents used were of analytical grade unless otherwise mentioned. Tri-n-butyl phosphate (TBP) used as the stationary phase was purified according to the procedure described by Hamlin *et al.*[7] Polyurethane foam, polyether of open cell-type, was used as the supporting material. It was a flexible polymer with 60 cells/cm on the average. This material was supplied by the North Hungarian Chemical Works, Sajóbábony, Hungary.

Column packing

A column of 1·5 cm bore and 15 cm length (with inlet and outlet taps at both ends) was used. The polyurethane packing material was washed 3 times with acetone. The dried material either in the form of small cubes or cylinders was equilibrated with purified TBP (3 ml per g of foam) with efficient stirring, then left overnight. The loaded foam was dried between two sheets of filter paper to remove excess of TBP. The cylindrical foam was cut such that each rod had a little larger diameter than that of the column. Either form of the loaded foam was evenly packed in the column by gentle pressure with a glass rod. This procedure reduced the volume of the compressed foam to one third of its original value. The packed column was evacuated by means of an oil-pump. Distilled water saturated with TBP was gradually allowed to fill the column through the outlet tap. This allows any residual air bubbles to escape from the foam inner surface to the top of the column and results in a homogeneous bed.

Procedure

Separation of Pd *and* Ni. The feed solution contained 1 ml of $PdCl_2$ solution (Pd 1 mg/ml), 1 ml of $NiCl_2$ solution (Ni 1 mg/ml) and 10 ml of $0{\cdot}1M$ perchloric acid containing 3% thiourea and 1% sodium perchlorate. Different experiments were made in which the concentration of Pd was kept constant while that of Ni was varied by a factor of up to 100.

Sorption of this mixture took place at a flow-rate of 1 ml/min. The mixture was chromatographed at flow-rates of 1–4 ml/min.

Water saturated with TBP was used as eluting solution. Ni was eluted with $0{\cdot}1M$ perchloric acid containing 3% thiourea and 1% sodium perchlorate, and Pd with water. In both cases the eluent was saturated with TBP, which served to keep the concentration of TBP on the foam material constant. Pd and Ni were determined spectrophotometrically as the Pd–thiourea and Ni–dimethylglyoxime complexes, at 292 and 366 nm respectively.

RESULTS AND DISCUSSION

Under the experimental conditions used Ni does not form a complex with thiourea,[17] and comes off the column in the first free column volumes without any measurable retention. On the other hand, Pd, which forms a complex with thiourea, was completely taken up by the loaded foam even in presence of 100 times its weight of Ni.

In comparison with published work[18] in which TBP was used as stationary phase loaded on different inert supports in granular form, it was found that polyurethane foam column support takes up TBP much more efficiently. For example, Kel-F takes up 1 ml of TBP per g, whereas polyurethane foam takes up 2 ml/g. This high uptake of stationary phase results in a high relative break-through capacity of the column, *i.e.*, ~30 mg of Pd^{2+} per g of coated foam.

Sharp and symmetrical peaks were obtained for both Ni and Pd. For Pd the height equivalent to one theoretical plate (HETP) was calculated to be ~1·4 mm.

The flow-rates were considerably higher than for granular supports,[15,18] without pressure applied at the top of the columns.

Institute of Inorganic and Analytical Chemistry,
L. Eötrös University, Budapest 8,
Muzeum krt. 4/6, Hungary.

T. BRAUN
A. B. FARAG

Summary—Foamed polymer is loaded with tributyl phosphate as stationary phase and compressed into a chromatographic column which will give flow rates of 1–4 ml/min, has a high break-through capacity and gives sharp and symmetrical peaks in elution chromatography. It has been applied to separation of nickel and palladium.

Zusammenfassung—Ein Polymerenschaum wird mit Tributylphosphat als stationärer Phase getränkt und in eine Chromatographiesäule gepreßt. Man erreicht Durchflußgeschwindigkeiten von 1–4 ml/min, eine hohe Durchbruchskapazität und bei der Elutionschromatographie scharfe und symmetrische Peaks. Das Verfahren wurde auf die Trennung von Nickel und Palladium angewandt.

Résumé—Un polymère-mousse chargé de phosphate de tributyle comme phase stationnaire et comprimé dans une colonne chromatographique qui donnera des vitesses d'écoulement de 1–4 ml/mn donne des pics accentués et symétriques en chromatographie d'élution. On l'a appliqué à la séparation du nickel et du palladium.

REFERENCES

1. I. Stronski, *Öster. Chem. Ztg.*, 1967, **68**, 5.
2. V. Speváčkova, *Chem. Listy*, 1968, **62**, 1194.
3. G. S. Katykhin, *Zh. Analit. Khim.*, 1965, **20**, 615.
4. C. Poitrenaud, *Chim. Anal.*, 1970, **52**, 39.
5. E. Cerrai and C. Testa, *J. Chromatog.*, 1962, **9**, 216.
6. W. Fletcher, *U.S. At. Energy. Comm. Rept.*, TID-7629, 276 (1961).
7. A. G. Hamlin, B. J. Roberts, W. Loughlin and S. G. Walker, *Anal. Chem.*, 1961, **33**, 1547.
8. J. S. Fritz and C. E. Hedrick, *Anal. Chem.*, 1962, **34**, 1411.
9. A. V. Kaljamin, *Radiokhimiya*, 1963, **5**, 749.
10. T. B. Pierce and P. F. Peck, *Nature*, 1962, **194**, 84.
11. H. Small, *J. Inorg. Nucl. Chem.*, 1961, **18**, 232.
12. V. A. Winsten, *Anal. Chem.*, 1962, **34**, 1334.
13. F. Nelson, *J. Chromatog.*, 1966, **20**, 378.
14. F. H. Ferrigno, *Rigid Plastics Foams*, Reinhold, New York, 1963.
15. H. J. M. Bowen, *J. Chem. Soc. A*, 1970, 1082.
16. M. Yusaf, Z. Sulcek and J. Doležal, *Anal. Lett.*, 1971, **4**, 119.
17. K. Swaminathan and H. M. N. H. Irving, *J. Inorg. Nucl. Chem.*, 1966, **28**, 171.
18. I. Akaza, T. Kiba and M. Taba, *Bull. Chem. Soc. Japan*, 1969, **42**, 1291.

Talanta, 1972, Vol. 19, p. 831. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Computer calculation of equilibrium constants using programme SCOGS. A further modification

SIR,

Further work by one of us (VSS) has shown that the correction recently published for programme SCOGS,[1] while mathematically more correct than that used in the original programme,[2] still requires a minor modification to one card of the programme. Statement No. 150, the derivation of calculated titre CTITR from known initial quantities and the measured pH, at present reads[1]

```
150 CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) − VOX1(K)*HO)/BA(K)
```

The quantity VOX1(K) (*i.e.*, current total volume at point K, equal to original volume plus added titrant) is correctly used in the term VOX1(K)*TURM(K) as the latter quantity, having earlier been corrected for volume change, must now be reduced to refer to original volume. No volume change appears in the term V(K)*AC(K). However the term VOX1(K)*HO contains the change in volume and this quantity should more correctly be assumed to be unknown and equal to CTITR. Thus the expression above ought to be written

```
CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) − V(K)*HO − CTITR*HO)/BA(K)
```

Rearranging gives the expression below and this should be substituted for Statement No. 150,

```
150 CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) − V(K)*HO)/(BA(K) + HO)
```

This modification, while advisable, has not made significant difference to the constants calculated to date.

I. G. SAYCE

Division of Inorganic and Metallic Structure
National Physical Laboratory
Teddington, Middlesex, U.K.

V. S. SHARMA

Department of Chemistry
Ohio State University
Columbus, Ohio, U.S.A.

20 *December* 1971

REFERENCES

1. I. G. Sayce, *Talanta*, 1970, **18**, 653.
2. *Idem, ibid.*, 1968, **15**, 1397.

Talanta, 1972, Vol. 19, p. 831. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Computer calculation of equilibrium constants using programme SCOGS. A further modification

SIR,

Further work by one of us (VSS) has shown that the correction recently published for programme SCOGS,[1] while mathematically more correct than that used in the original programme,[2] still requires a minor modification to one card of the programme. Statement No. 150, the derivation of calculated titre CTITR from known initial quantities and the measured pH, at present reads[1]

```
150 CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) – VOX1(K)*HO)/BA(K)
```

The quantity VOX1(K) (*i.e.*, current total volume at point K, equal to original volume plus added titrant) is correctly used in the term VOX1(K)*TURM(K) as the latter quantity, having earlier been corrected for volume change, must now be reduced to refer to original volume. No volume change appears in the term V(K)*AC(K). However the term VOX1(K)*HO contains the change in volume and this quantity should more correctly be assumed to be unknown and equal to CTITR. Thus the expression above ought to be written

```
CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) – V(K)*HO – CTITR*HO)/BA(K)
```

Rearranging gives the expression below and this should be substituted for Statement No. 150,

```
150 CTITR = (VOX1(K)*TURM(K) + V(K)*AC(K) – V(K)*HO)/(BA(K) + HO)
```

This modification, while advisable, has not made significant difference to the constants calculated to date.

I. G. SAYCE

Division of Inorganic and Metallic Structure
National Physical Laboratory
Teddington, Middlesex, U.K.

V. S. SHARMA

Department of Chemistry
Ohio State University
Columbus, Ohio, U.S.A.

20 *December* 1971

REFERENCES

1. I. G. Sayce, *Talanta*, 1970, **18**, 653.
2. *Idem, ibid.*, 1968, **15**, 1397.

Talanta, 1972, Vol. 19, pp. 833 to 838. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF TRACE ELEMENTS IN METALS AND ALLOYS BY ATOMIC-ABSORPTION SPECTROSCOPY USING AN INDUCTION-HEATED GRAPHITE WELL FURNACE AS ATOM SOURCE

J. B. HEADRIDGE and DAVID RISSON SMITH
Chemistry Department, Sheffield University, Sheffield, U.K.

(*Received* 19 *August* 1971. *Accepted* 29 *October* 1971)

Summary—An induction-heated graphite furnace, coupled to a Unicam SP 90 atomic-absorption spectrometer, is described for the direct determination of trace elements in metals and alloys. The furnace is capable of operation at temperatures up to 2400°, and has been used to obtain calibration graphs for the determination of ppm quantities of bismuth in lead-base alloys, cast irons and stainless steels, and for the determination of cadmium at the ppm level in zinc-base alloys. Milligram samples of the alloys were atomized directly. Calibration graphs for the determination of the elements in solutions were obtained for comparison. The accuracy and precision of the determination are presented and discussed.

IN RECENT years much interest has been shown in the development of non-flame methods of atomization for atomic-absorption spectroscopy.[1] Many such atomization methods have been reported but few have dealt with systems suitable for direct analysis of solid samples. The authors have previously reported on an induction furnace for the direct determination of trace elements by atomic-absorption spectroscopy using the solid sample directly.[2] The results obtained were very encouraging and it was decided that further investigations on a similar atomizer should be continued. The major disadvantage of the system described previously was that, since alumina sheathing was used, the operating temperature was limited to approximately 1900°. A furnace, based on a system commonly used for vacuum fusion, and capable of operation up to 2400°, was thus constructed, and the application of this furnace to atomic-absorption spectroscopic determination of trace elements is reported.

EXPERIMENTAL

Apparatus

A diagram of the furnace is shown in Fig. 1. The carbon core consisted of a cylinder of graphite, 120 mm long and 38 mm in diameter, with a 13 mm hole bored centrally along its length to within 10 mm of one end. Light-guides, consisting of graphite tubes 75 mm long, 15 mm outside diameter and with a 6 mm bore, were positioned at each side of the core, centred on a point 50 mm from the base (closed end). Acheson e.g.w. grade graphite was used in this construction.

The core was held in a quartz tube, 130 mm long and 47 mm internal diameter, with side-arms, 50 mm long and 18 mm internal diameter to cover the light-guides. The side-arms were tapered at their ends to give a tight fit on the light-guides. The space between the graphite core and quartz sheathing was packed with insulating graphite, 300 mesh.

The core was heated by a six-turn induction coil wound round the quartz sheathing as shown in the diagram, the power to the coil being supplied by a 6 kW Radyne Induction Generator.

The whole of this was seated on an asbestos work-table and enclosed by an asbestos box which was sealed to the table with refractory cement. The box had gas inlet and outlet points so that the system could be flushed out and operated in an inert gas atmosphere. Argon was used in these experiments. "Spectrosil" windows, 40 mm in diameter, were fitted in two sides of the asbestos box, in line with the light-guides to allow the passage of light through the cell.

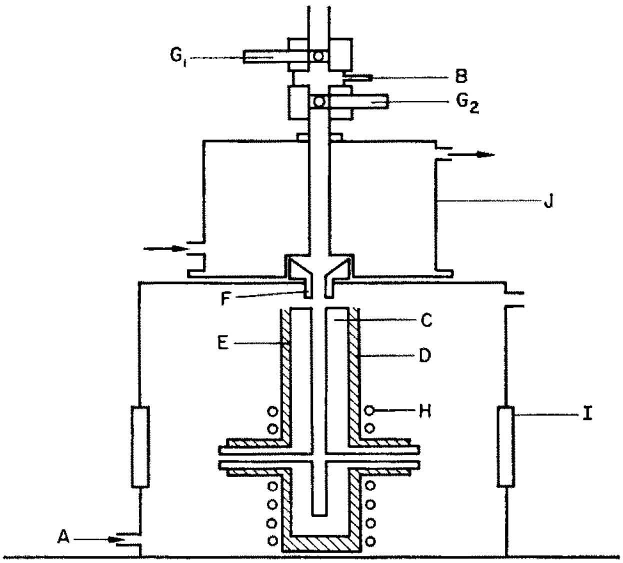


FIG. 1.—Induction-heated graphite furnace for atomic-absorption spectroscopy. *A*, Argon inlet; *B*, argon inlet; *C*, graphite core; *D*, quartz sheath; *E*, graphite insulation; *F*, graphite funnel; G_1 and G_2, Econ-O-Miser ball valves type 44/46/T (Worcester Valve Co. Ltd.) of 13-mm nominal bore; *H*, induction coil; *I*, "Spectrosil" windows; *J*, aluminium cooling jacket with cold water circulating through it.

Samples were introduced into the furnace from above *via* a double valve arrangement which prevented the introduction of air along with the sample. A graphite funnel was positioned in the top of the asbestos box, directly above the bore in the graphite core, to guide the samples into the hot core. A hollow aluminium cooling unit was designed to fit under the valves and over the graphite funnel, and was secured to the lid of the asbestos box. This was necessary to prevent heat from the furnace destroying the Teflon valve seats and seals.

Radiation was provided by electrodeless discharge tubes. These were powered by a Microtron 200 microwave generator, fitted with a voltage stabilizing unit and frequency modulator unit operating at 50 Hz. A Unicam SP 90 atomic-absorption spectrophotometer was used as detector and amplification unit, the output signal being obtained on a Honeywell 10 mV recorder, fast-response type.

Preliminary investigations

To obtain maximum sensitivity of the atomic-absorption determination when using a system such as that described above, it is necessary, particularly when a peak-height method of absorbance measurement is used, that all the atoms of the element of interest appear in the light-path in a short period of time. Thus when solid samples were used, sensitivity was expected to be dependent upon the furnace temperature, and preliminary experiments were carried out to investigate this point. These indicated that the optimum temperature is one just above the boiling point of the matrix element, provided the element of interest is also volatile at this temperature.

Should the element to be determined be less volatile than the matrix element, a temperature just above the boiling point of the trace element should be used. When the matrix element is not in the gaseous phase at the maximum temperature of the furnace, suitable calibration graphs can still be obtained provided that the matrix element is molten and the element of interest is volatile.

A similar series of experiments was carried out to investigate the effect of varying the argon gas flow. Maximum sensitivity was obtained when the argon flow was stopped just before introduction of the sample into the furnace, the flow being restored after the peak, to flush metal vapour from the cell.

General procedure

The argon flow through inlet *A* was adjusted to 10 l./min to flush out the system. The Radyne generator was adjusted to bring the furnace to a suitable temperature and the argon flow was adjusted to 7 l. min. Valve G_1 was opened and a sample was introduced into the sample tube (see Note).

Argon inlet *B* was opened and a flow of 2 l. min was used to flush out air from the sample tube. Valve G_1 and argon inlet *B* were then closed.

The controls of the SP 90 were adjusted to give a transmission setting of 100% on the recorder. The argon supply was stopped by closing argon inlet *A*, and valve G_2 was opened and closed quickly to allow the sample to fall into the "well" furnace. After recording of a minimum transmission reading, argon inlet *A* was opened and an argon flow of 7 l. min was used to flush out the system.

Once the base-line for 100% transmission had again been achieved, the procedure was repeated for the next sample.

Note. In analysis for trace elements directly on solid samples, small pieces of the materials under study (mg samples) were introduced into the furnace. These materials were alloys which contained traces of elements of which the concentrations had been determined by well-established analytical methods. For solution analysis, small volumes were dispensed by micrometer syringe and were collected on carbon pellets 6 mm in diameter and 3 mm in depth. After evaporation of the solvent, to produce a solid deposit of the salt, the carbon pellets were added to the furnace as described above. Standard solutions of the metals were prepared by dissolving the metals in nitric acid.

RESULTS

Calibration graphs for the determination of cadmium in zinc-base alloys (curve *A*) and solutions (curve *B*), using the 228·8-nm line and furnace temperatures of 1050° and 2300° respectively are shown in Fig. 2. A temperature of 2300° was used to ensure dissociation of any molecular species of cadmium formed from cadmium nitrate. The sensitivities (1% absorption values) calculated from these graphs were 0·40 ng for cadmium from zinc-base alloys and 0·62 ng for cadmium from solution. As 5-mg samples of zinc-base alloys were used, the 1% absorption value for cadmium in zinc-base alloys corresponds to a concentration of 0·08 μg/g.

Calibration graphs for the determination of bismuth in lead-base alloys, stainless steels, cast irons and solutions are shown in Figs. 3 and 4 respectively. The resonance

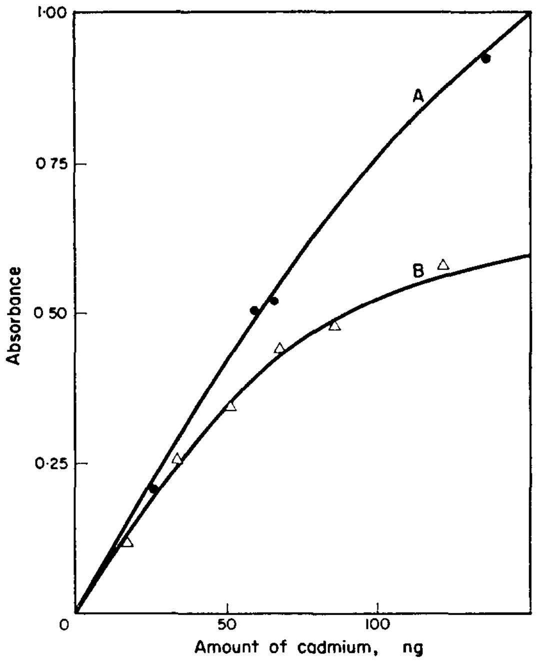


Fig. 2.—Calibration graphs for the determination of cadmium in (*A*) zinc-base alloys and (*B*) solutions.

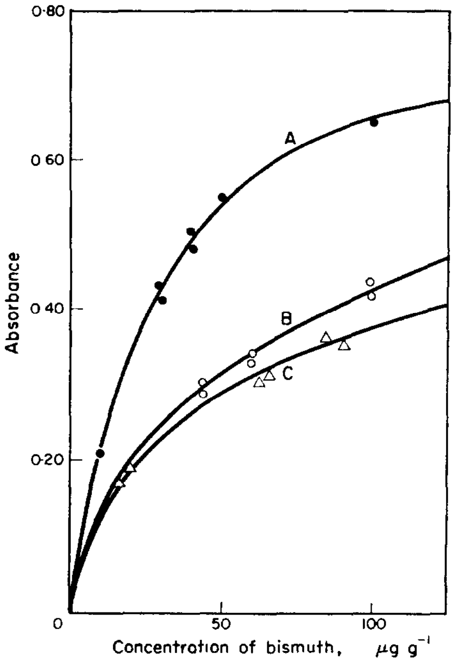


FIG. 3.—Calibration graphs for the determination of bismuth in (*A*) lead-base alloys; (*B*) stainless steels and (*C*) cast irons.

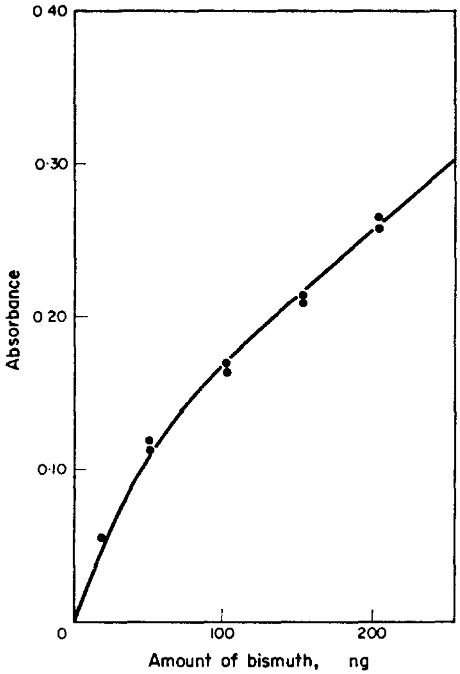


FIG. 4.—Calibration graph for the determination of bismuth in solution.

line at 306·8 nm was used in all cases. A furnace temperature of 1775° was employed for the lead-base alloys, all other determinations being carried out at 2400°. All the graphs in Fig. 3 have been obtained for solid samples and the abscissa conveniently shows the concentration of bismuth (μg/g) in the 6-mg samples used. The 1% absorption values calculated from the calibration graphs were 0·24 μg/g for bismuth from lead-base alloys, 0·30 μg/g for bismuth from stainless steels and 0·33 μg/g for bismuth from cast irons. Since the weights of sample used were 6 mg, these 1% absorption values correspond to amounts of bismuth of 1·4 ng for lead-base alloys, 1·8 ng for stainless steels and 2·0 ng for cast irons. By comparison the 1% absorption value for bismuth from solution, calculated from Fig. 4, was 1·4 ng.

Accuracy and precision data obtained for the determination of bismuth in lead-base alloys and cast irons, together with corresponding figures for the determination of cadmium in zinc-base alloys are summarized in Table I. In order to obtain these results, a sample of the appropriate alloy, not used in the preparation of the calibration graph, was analysed a number of times by the procedure given, the concentrations being read off the calibration graph.

TABLE I.—ACCURACY AND PRECISION OF ANALYSES USING GRAPHITE INDUCTION FURNACE

Determination	No. of samples analysed	Concentration of trace element determined μg/g		Relative standard deviation %
		This method	Independent method	
Bi in lead-base alloy	10	43	40	8·1
Bi in cast iron	10	66	63	8·1
Cd in zinc-base alloy	6	12·7	13·0	3·6*

* These samples were weighed on a semimicro 5-place balance; other samples were weighed on a 4-place laboratory balance.

DISCUSSION

The results obtained for the determination of bismuth and cadmium in various matrices were considered to be satisfactory, the accuracy and precision of the determinations using the graphite "well" furnace being quite comparable with those obtained by other workers on furnace systems. As indicated in Table I, weighing errors can account for a considerable proportion of the error and, if more sensitive balances are used, the precision can be improved.

All the calibration graphs are curved, and this is thought to be due mainly to a sluggish response of the amplification system to a rapidly changing signal. This becomes particularly noticeable when a peak-height method of absorbance measurement is used. Since distortion of the peak height will increase as the height of the peak increases, curved calibration graphs result.

The decrease in sensitivity of bismuth determination from lead-base alloys to cast irons and stainless steels is due to the use of a peak-height method of absorbance measurement. Since the maximum temperature available was not above the boiling point of the base element in the last two types of sample, vaporization of the trace element of interest was not so rapid. The absorption peaks were shallower and broader than those obtained with the more volatile base materials. Use of an integration method of absorbance measurement would probably overcome this lack of sensitivity.

Although the sensitivities obtained by using the graphite "well" furnace are not so good as those obtained with the horizontal furnace described previously,[2] it is felt that this furnace does have a future. It appears particularly useful for the determination of trace elements at the ppm level, using the solid sample directly.

Initial determinations of tin at the ppm level in lead-base alloys and aluminium-base alloys have also been carried out successfully. The furnace appears suitable for the determination of many elements, including Ag, As, Ca, Hg, Mg, Mn, Pb, Sb and Zn, in a wide range of matrices. Whilst the accuracy and precision values so far obtained by this technique may not be acceptable for the most exacting determinations at the ppm level, the technique could prove very useful as an analytical tool for rapid semi-quantitative analysis.

Acknowledgements—One of the authors (D. R. S.) thanks the Science Research Council for a Studentship to undertake this work. The authors are indebted to B.I.S.R.A. and B.C.I.R.A. for provision of samples and to Mr. W. R. Nall of Bragg Laboratory, Sheffield for discussion in connection with certain samples.

Zusammenfassung—Ein an ein Unicam SP 90-Atomabsorptionsspektrometer gekoppelter Graphit-Induktionsofen wird beschrieben, der zur direkten Bestimmung von Spurenelementen in Metallen und Legierungen dient. Der Ofen kann bei Temperaturen bis 2400° betrieben werden und wurde verwendet zur Aufstellung von Eichkurven zur Bestimmung von ppm-Mengen Wismut in Legierungen mit Blei als Grundmetall und zur Bestimmung von Cadmium im ppm-Bereich in Legierungen auf Zinkbasis. Milligramm-Proben der Legierungen wurden direkt in den atomaren Zustand überführt. Zum Vergleich wurden Eichkurven zur Bestimmung der Elemente in Lösung aufgenommen. Genauigkeit und Richtigkeit der Bestimmung werden angegeben un diskutiert.

Résumé—On décrit un four de graphite chauffé par induction et couplé à un spectromètre d'absorption atomique Unicam SP 90 pour le dosage direct de traces d'éléments dans les métaux et alliages. Le four est capable d'opérer à des températures allant jusau'á 2400°, et a été utilisé pour obtenir des courbes d'étalonnage pour le dosage de quantités de l'ordre du ppm de bismuth dans des alliages à base de plomb, des fontes et des aciers inoxydables, et pour le dosage du cadmium au niveau de la ppm dans des alliages à base de zinc. Des échantillons des alliages, de l'ordre du milligramme, ont été atomisés directement. Les courbes d'étalonnage pour le dosage des éléments en solutions ont été obtenues pour comparaison. On présente la précision et la fidélité du dosage et en discute.

REFERENCES

1. V. G. Mossotti and K. Laqua, *Spectrochim. Acta*, 1967, **23B**, 197.
2. J. B. Headridge and D. R. Smith, *Talanta*, 1971, **18**, 247.

Talanta, 1972, Vol. 19, pp. 839 to 850. Pergamon Press. Printed in Northern Ireland

SEPARATION OF THE NON-VOLATILE NOBLE METALS BY REVERSED-PHASE EXTRACTION CHROMATOGRAPHY

CHRISTEL POHLANDT and T. W. STEELE
National Institute for Metallurgy, Private Bag 6, Johannesburg, South Africa

(*Received* 15 *July* 1971. *Accepted* 4 *November* 1971)

Summary—The procedure involves the use of tri-n-butyl phosphate (TBP) adsorbed by Porasil C and stepwise elution with sulphuric acid and hydrochloric acid. The distribution coefficients for the two systems (TBP and hydrochloric acid and TBP and sulphuric acid) and the elution characteristics were studied. A description is given of a procedure applicable to the analysis of prills obtained from the fire assay of platinum-bearing ores.

ION-EXCHANGE[1–4] and chromatographic techniques[5,6] have been applied in the search for better and faster separation methods for multicomponent mixtures of the noble metals. A useful contribution in this field has been the work of Kember and Wells,[7] who describe the separation of microgram amounts of platinum, palladium, rhodium and iridium by chromatographic procedures on paper strips. James[8] examined their procedure for the separation of platinum and palladium, and, after making modifications to the apparatus, applied the method to the separation of platinum and palladium in silver prills obtained from ore samples by the conventional fire-assay technique.

This procedure and a modified procedure of Kember and Wells for rhodium and iridium[9] were applied at the National Institute for Metallurgy to the analysis of prills obtained from the fire assay of samples of ore from the Merensky Reef. Although the results obtained for platinum and palladium compared favourably with the results obtained by atomic-absorption methods, the procedure was found to be tedious and time-consuming. Moreover, the very small amount of sample solution that could be applied to a paper strip often made the determination of rhodium and iridium in low concentrations very difficult.

Because of these disadvantages, it was decided to explore the related technique of reversed-phase extraction chromatography (RPEC). This technique combines the selectivity of many organic extractants with the multistage character of chromatography, and should be applicable to the separation of noble metals from one another and from base metals. Columns permit the use of much larger volumes of sample solution, thus facilitating the determination of the separated noble metals.

From reviews published by Eschrich and Drent[10] and by Cerrai and Ghersini,[11] it is apparent that a number of papers on the separation of the noble metals have been published. It was decided that the use of tri-n-butyl phosphate (TBP) as a stationary phase should be investigated. Contradictory statements had been made, particularly about R_f values for the noble metals in the system TBP and hydrochloric acid.[12–15] The distribution coefficients for noble metals and for several base metals commonly associated with noble metals in ores and concentrates were therefore determined under conditions appropriate to RPEC on columns by use of the TBP and hydrochloric acid system. The distribution coefficients for the system TBP and sulphuric acid were also determined. These determinations were followed by extensive elution studies in an attempt to achieve a separation of platinum, palladium, rhodium, iridium and gold, and to develop a working procedure applicable to cupellation prills obtained from the fire assay of ores, to hydrochloric acid solutions of the noble metals obtained from the dissolution of tin and nickel sulphide buttons, and to acid extracts and concentrates of samples from the Merensky Reef.

EXPERIMENTAL

Standard solutions of noble metals

Standard solutions of platinum (10·0 mg/ml) *and palladium* (1·0 mg/ml). Prepared by dissolution of the metals in *aqua regia*. After evaporation and repeated treatment with hydrochloric acid, the residues were dissolved in 50% v/v hydrochloric acid.

Standard gold solution, 1·0 *mg/ml.* Prepared by dissolving gold in *aqua regia.*

Standard solutions of rhodium, iridium, ruthenium, and osmium were prepared by dissolution of an amount of their "Specpure" ammonium salts representing 0·1000 g of the metal, in a mixture of hydrochloric acid and nitric acid. After removal of the nitric acid by repeated treatment with concentrated hydrochloric acid, the salts were dissolved in 50% v/v hydrochloric acid to give solutions containing 1·0 mg of metal/ml. The composition of the ammonium salts of rhodium, iridium and ruthenium is not strictly stoichiometric, and the percentage of the metal in the salt was determined after reduction of a known amount of salt to the metal with burning hydrogen. From the weight of metal obtained, its content in the salt was calculated.

Determination of the noble metals

It was found convenient to monitor the elution during chromatographic separations by continuous photometric measurement of the eluate. A Zeiss spectrophotometer (model PMQII) and a "Rikadenki" recorder were used for this purpose, and the absorbance was measured at 300 nm. Although the sensitivity for iridium was poor, rhodium, platinum and palladium were readily detectable.

This detection method is not selective for the platinum-group metals, but it served as a useful indication of changes in the concentration of an individual metal in the eluate, thereby considerably reducing the time required for the subsequent analysis.

Platinum in individual eluate fractions was determined by measurement of its tin(II) chloride complex[7] at 403 nm. Palladium was determined photometrically with thioglycollic acid,[7] and gold in inorganic and organic solutions was measured by atomic-absorption spectrometry. Rhodium in sulphuric acid solutions was determined by a modified method of Khattak and Magee,[16] based on the formation of the yellow rhodium(III)–tin(II) chloride complex in concentrated hydrochloric acid, followed by the extraction of this complex into an amine solution and the measurement of the organic phase at 415 nm. This extraction method effectively eliminates interference by base metals, 1-mg amounts of the following ions having been tested and found not to interfere: iron(III), lead, nickel, copper(II), and cobalt(II). Sulphate, chloride and nitrate do not interfere.

The method used for the photometric determination of iridium in hydrochloric acid solutions is a modification of that developed by Ayres and Bolleter,[17] in which leuco-Crystal Violet is oxidized to its coloured form by iridium(IV).

Distribution coefficients

Kel-F powder was used as the inert support for TBP for the determination of the distribution coefficients. However, because Kel-F powder was found to vary in absorption properties and appearance from batch to batch, it was replaced by Porasil C for the subsequent elution studies.

The solvent capacity of the different supports was determined by a standard method proposed by Pietrzyk.[18] Different batches of Porasil C absorbed 43·6–44·0% of the TBP, compared with the 1·6–35·0% absorbed by Kel-F powder. In later experiments Porasil C having a TBP content of 25% by weight was used on the assumption that the E_{a}° values would not be altered by the change of support. The mixture had the properties of a dry, free-flowing powder, whereas Kel-F powder containing the same amount of TBP was a sticky mass. The TBP-treated Kel-F powder was mixed with the extractant dissolved in chloroform and the chloroform was allowed to evaporate.

Aliquot portions (10 ml each) of standard solutions containing 100–500 ppm of metal and varying concentrations of hydrochloric and sulphuric acids were shaken with 1 g of TBP-treated Kel-F powder in a stoppered glass bottle for 3 hr. After equilibration the aqueous phase was analysed, and the distribution coefficients were calculated according to the equation:

$$E_a^\circ = \frac{\text{concentration of metal in organic phase} \times \text{vol. of solution}}{\text{TBP-treated Kel-F powder (g)} \times \text{concentration of metal in aqueous phase}}.$$

To determine the time needed for equilibrium to be reached, 10 ml portions of 6*M* hydrochloric acid, containing 100 ppm of platinum, were shaken with treated Kel-F for 0·5–8 hr. Constant results were obtained after 2 hr.

The concentration of metals in the aqueous phase was determined by atomic-absorption spectrometry, spectrophotometry (iridium) and isotopic measurements (osmium, ruthenium and silver). The distribution coefficients for the noble metals for the system TBP and sulphuric acid were determined, where necessary, in the presence of trace amounts of hydrochloric acid to prevent losses by precipitation. For osmium and ruthenium, the respective chloride tracer was added to the sulphuric acid solutions. In an attempt to ensure that the noble metals were in their oxidized state, solutions were used that had previously been oxidized with sodium chlorate. The results are given in Table I.

Platinum(IV) and osmium have almost identical distribution coefficients and are thus not separable. However, it should be possible for these metals together to be separated from the other four platinum-group metals when hydrochloric acid (3–6*M*) is used as eluent. Rhodium and palladium cannot be separated, but both metals could perhaps be separated from iridium with hydrochloric acid ranging from 3 to 5*M* if the column were long enough. As aluminium, chromium, cobalt, nickel, copper and manganese are only very slightly retained, they can be separated from iron, gold, osmium, platinum and iridium. The platinum-group metals can be separated from gold by elution with 1–11*M* hydrochloric acid.

Distribution coefficients for the platinum-group metals in sulphuric acid (Table II) are distinctly higher than in hydrochloric acid solutions, and separation factors between the individual noble metals differ sufficiently for separation to be made. Gold has distribution coefficients higher than 10^4 and can therefore easily be separated from all the other noble metals. The base metals, including iron and tin, are not significantly retained and can be separated from all the noble metals with the possible exception of rhodium and ruthenium.

Although R_f values are not strictly comparable with E_a° values, it is noted that the values in Table I do not agree with the R_f values obtained by Bark *et al.*[12] for osmium, molybdenum, silver and to a lesser extent, palladium. The values in this table also do not correspond with the R_f values quoted by Volynets *et al.*,[15] who give values of 0·07 and 0·06 for platinum and iridium with 4*M* hydrochloric acid as the mobile phase. Similarly our values show that rhodium and palladium could not be separated on a column with 4–5*M* hydrochloric acid, which is contrary to Bark *et al.*[13] and Volynets *et al.*[15] The low E_a° value for platinum in 9*M* hydrochloric acid in Table I does not agree with the zero R_f value given by O'Laughlin[14] for platinum on TBP-treated paper with 9*M* hydrochloric acid as the mobile phase.

However, the results presented in Tables I and II are in good agreement with the liquid-liquid-extraction results published by Ishimori *et al.*[19] for both hydrochloric acid and sulphuric acid solutions. The few exceptions—mainly for the noble metals—may be due to different oxidation states of the noble metals.

Elution studies

To verify the conclusions drawn from the distribution coefficients, elution studies with mixed noble-metal solutions on columns 10 cm in length were carried out. Since one of the objectives of the project was to develop a separation technique applicable to prills obtained by fire assay, ruthenium and osmium were omitted from all further experiments; they would be volatilised during dissolution and evaporation of samples with *aqua regia* in the presence of an oxidizing agent. As can be seen from Fig. 1, when 5*M* hydrochloric acid was used as the eluent, palladium and rhodium were readily eluted together, and were thus separated from platinum and iridium, which move much more slowly. Although an oxidizing agent (sodium chlorate) had been added to the hydrochloric acid solution and the platinum(IV) was expected to be eluted after the iridium, the platinum was eluted first. The platinum behaved as if it were in the reduced state and moved in accordance with the distribution coefficients for platinum(II). It appears that, in the absence of an oxidizing environment and possibly because of reducing impurities in the TBP-treated Porasil C, the platinum(IV) can be reduced after it has been transferred to the column. This hypothesis is supported by the observation that platinum(II) in hydrochloric acid solution moves at the same rate as platinum(IV) under the conditions described. When 4*M* sulphuric acid was used as the eluent, rhodium was clearly separated from the other metals, and platinum and iridium both showed extensive tailing (Fig. 2). All attempts to achieve better resolution of the peaks and less tailing were unsuccessful. These attempts included variations in

TABLE I.—E_a° VALUES OF METAL CHLORIDES FOR THE SYSTEM TBP AND HYDROCHLORIC ACID

Metal	Acid concentration, *M*										
	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0	11·0
Pt(II)	1·2	2·5	4·5	6·4	5·8	3·8	2·4	3·0	2·4	1·6	1·3
Pt(IV)	5·0	12·0	17·0	19·0	16·0	11·8	7·2	5·4	4·3	3·8	3·7
Ir(IV)	1·3	3·4	6·2	7·4	7·4	6·6	4·0	2·2	1·4	0·5	0·3
Os(IV)	10·5	16·0	18·0	18·0	16·0	12·0	8·8	7·0	4·2	3·6	3·4
Pd(IV)	<0·5	<1·0	1·2	1·5	1·5	1·4	1·3	1·2	1·2	1·3	1·4
Ru(III)	1·7	1·9	1·8	1·5	1·2	0·8	<0·5	<0·5	<0·5	<0·5	<0·5
Rh(III)	0·3	0·7	0·9	1·2	1·5	1·7	2·0	2·0	1·8	1·7	1·7
Sn(II)	45·0	140	330	500	498	370	210	100	45	22	10
Ni(II)						Negligible adsorption					
Cu(II)						Negligible adsorption					
Co(II)						Negligible adsorption				<0·5	<0·5
Mn(II)						No adsorption					
Fe(III)	0·6	10·0	45	200	2000	6000	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Mo(VI)	0·5	7·0	52	120	160	170	140	110	88	*	*
Cr(III)	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	0·26	0·36	0·47
Ag(I)	2·8	2·4	1·5	1·0	0·4	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1
Au(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Al(III)	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1
Hf(IV)	0·7	0·35	0·25	0·22	0·25	0·4	1·5	70	520	$>10^3$	$>10^3$
Zr(IV)	1·2	0·45	0·35	0·35	0·4	0·9	11	200	$>10^3$	$>10^3$	$>10^3$
U(VI)	*	0·6	3·2	7·8	16	22	25	24	19	11	8
Th(IV)	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	<0·1	0·2	0·86	1·7

* not determined

TABLE II.—E_a° VALUES OF METALS FOR THE SYSTEM TBP AND SULPHURIC ACID

Metal	Acid concentration *M*						
	0·5	1·0	2·0	3·0	4·0	5·0	6·0
Pt(IV)	2·6	4·5	15·0	29·0	40·0	39·0	26·0
Ir(IV)	8·6	6·0	15·0	30·0	60·0	125·0	160·0
Os(IV)	10·0	16·0	36·0	64·0	83·0	90·0	86·0
Pd(IV)	1·4	3·2	12·5	32·0	72·0	145	300
Ru(III)	0·28	0·9	3·0	3·9	4·0	4·0	3·3
Rh(III)	1·9	2·4	3·8	5·0	2·8	N.D.	N.D.
Sn(IV)	<0·1	<0·1	1·8	3·4	5·4	8·8	13·5
Sn(II)	N.D.	N.D.	0·4	0·6	1·4	2·2	3·9
Ni(II)			Negligible adsorption				
Cu(II)			Negligible adsorption				
Co(II)			Negligible adsorption				
Mn(II)			Negligible adsorption				
Fe(III)			Negligible adsorption				
Mo(VI)	<0·1	0·25	1·1	2·9	4·8	*N.D.	*N.D.
Cr(III)			Negligible adsorption				
Ag(I)	10·0	14·0	25·0	40·0	45·0	38·0	26·0
Au(III)	>10^4	>10^4	>10^4	>10^4	>10^4	>10^4	>10^4
Al(III)			Negligible adsorption				
Hf(IV)	<0·5	<0·5	<0·5	<0·5	<0·5	<0·5	<0·5
Zr(IV)			Negligible adsorption				
U(VI)			Negligible adsorption				
Th(IV)	0·2	0·5	0·6	0·4	0·8	N.D.	N.D.
Te(IV)			Negligible adsorption				
Se(IV)	<0·5	<0·5	<0·5	<0·5	<0·5	<0·5	<0·5

* not determined

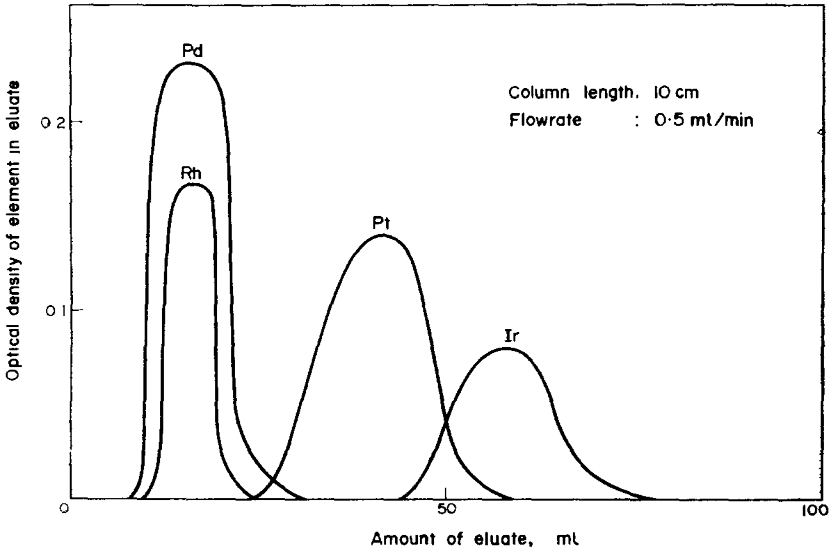


FIG. 1.—Elution of the noble metals with 5*M* hydrochloric acid.

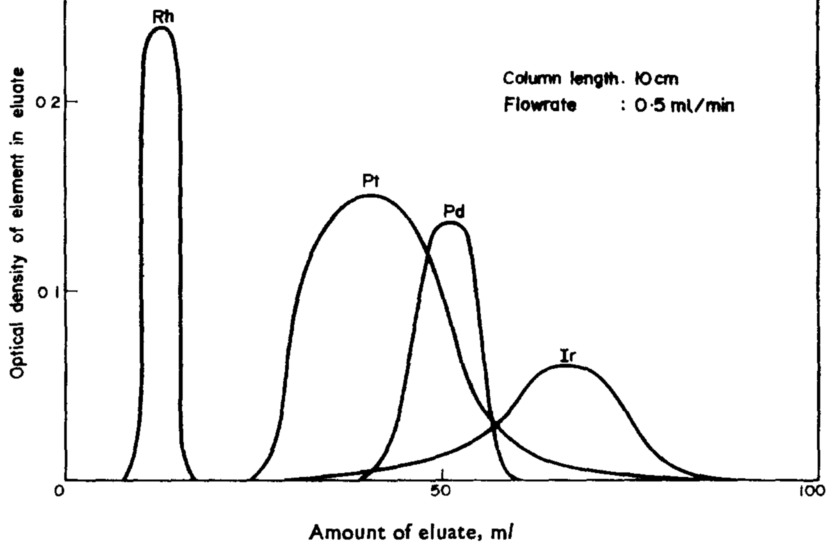


FIG. 2.—Elution of the noble metals with 4*M* sulphuric acid.

the flow-rate, the acid concentration of the eluent, the length of the column, and the amount of oxidizing agent (sodium chlorate) both in the sample solution and in the eluent.

From the two systems studied it became clear that the non-volatile noble metals could not be separated by the use of a single acid system. However, a combination of two systems, *i.e.*, the introduction of stepwise elution on a column bed 30 cm in length, produced the elution curves shown in Fig. 3. Rhodium (and base metals) were sharply separated from palladium by elution with 4*M* sulphuric acid, and palladium was completely separated from platinum by elution with 5*M* hydrochloric

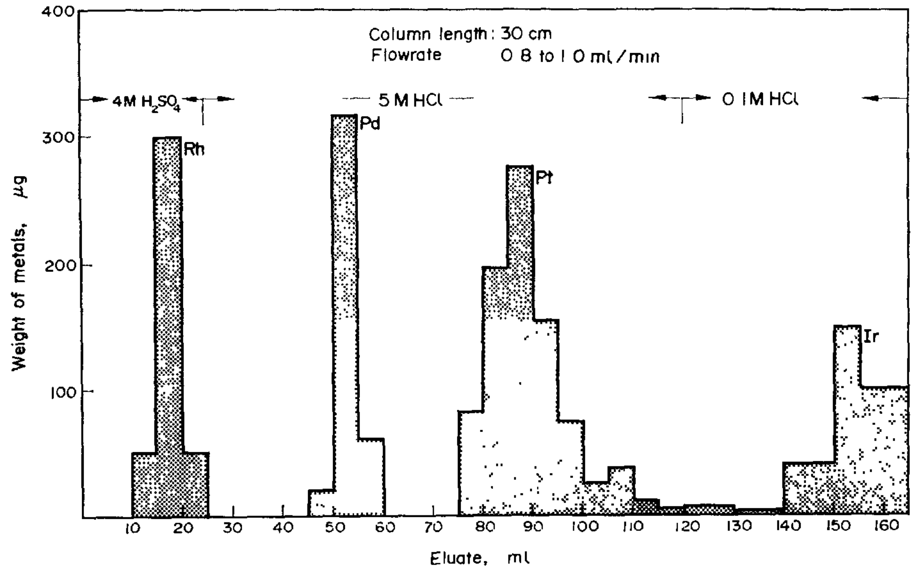


FIG. 3.—Reversed-phase chromatographic separation of the platinum group metals.

acid. After elution of the platinum with 5*M* hydrochloric acid, the iridium was eluted with 0·1*M* hydrochloric acid to increase its elution rate. Gold was completely separated from all the other metals and remained on the column.

Because the elution peaks of platinum and iridium were clearly separated when 5*M* hydrochloric acid was used as eluent, it was thought that a complete separation could be achieved by the variations previously attempted to achieve better resolution of the peaks. However, platinum invariably formed two bands (Fig. 4); the first—probably platinum(II)—representing 90–95% of the platinum present, moved considerably faster than the iridium, the second—probably platinum(IV)—moved at a slower rate than the iridium. Iridium, in the absence of platinum, formed two bands that moved at a much slower rate than platinum and could conveniently be eluted together with 0·1*M* hydrochloric acid. In the presence of platinum, it formed a third band, which was eluted in the fraction containing the bulk of the platinum. The amount of iridium in this fraction represented between 5 and 20% of the total iridium, depending on the amount of platinum present. It was thus concluded that the presence of the one metal affected the behavior of the other.

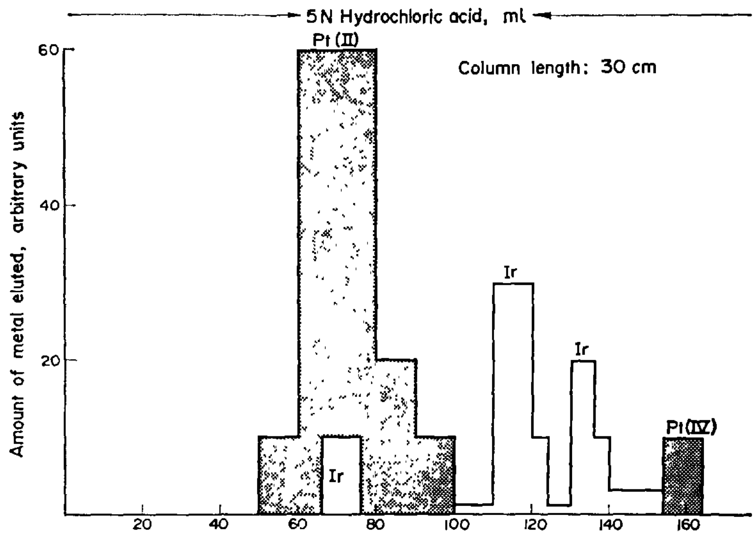


FIG. 4.—Elution of platinum and iridium under oxidizing conditions.

In an attempt to inhibit the formation of overlapping bands, varying amounts of oxidizing agents were added to the sample solution and to the eluent. Only sodium nitrate, added in milligram amounts, eliminated these effects for platinum, possibly because the platinum(IV) was reduced to platinum(II) by traces of nitrite impurities. The addition of nitrate had no effect in the presence of iridium, but it suggested that the presence of reducing agents might be beneficial.

Separation of platinum and iridium under reducing conditions

Platinum and iridium in a mixed solution of hydrochloric and sulphuric acids (2·5*M* and 4*M* respectively) were reduced with either sodium nitrite or sodium sulphite before the chromatographic separations, 5*M* hydrochloric acid being used as the eluting agent. Iridium under reducing conditions moved considerably faster than platinum, which apparently was not affected. However, the recovery of iridium in the eluate, when nitrite was used as reducing agent, was found to be poor and not reproducible. The addition of sodium sulphite to the sample solution gave a quantitative separation of iridium from platinum (Fig. 5).

After elution of the iridium with 5*M* hydrochloric acid, the platinum can be eluted with water to increase its elution rate. The effect of varying amounts of sulphite is shown in Table III. To ensure an excess of sulphite, it was decided that 20 mg of sodium sulphite should be added to the solution.

Separation of gold

After separation of the base metals and platinum-group metals from gold by separate elutions with 4*M* sulphuric acid, 5*M* hydrochloric acid, and 0·1*M* hydrochloric acid, the gold can be eluted from the column with 14*M* nitric acid.[20] Since this approach is unpleasant and time-consuming and

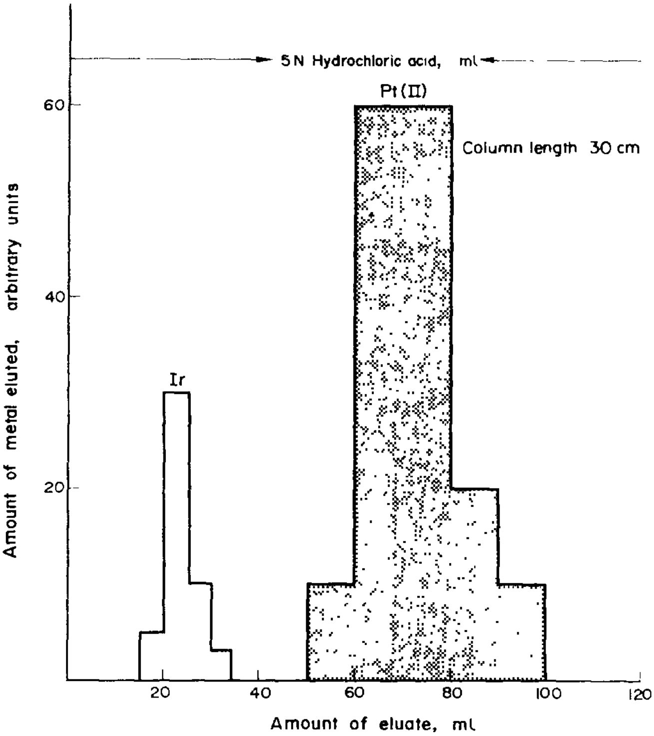


FIG. 5.—Elution of platinum and iridium under reducing conditions.

TABLE III.—THE EFFECT OF VARYING AMOUNTS OF SODIUM SULPHITE ON THE SEPARATION OF IRIDIUM FROM PLATINUM

Sodium sulphite added *mg*	Iridium added *μg*	Iridium recovered *μg*	Platinum added *μg*	Platinum recovered *μg*
10	75	73·5	1000	986
15	75	73·0	1000	987
20	100	95·0	1000	980
25	100	93·0	1000	989
50	100	95·5	1000	986

reduces the life of the column because of losses of TBP, it was considered advisable to conduct the separation of gold on a separate small column. That the recovery of gold is quantitative under these conditions is shown in Table IV.

Amounts of metals that can be separated

Varying ratios of non-volatile noble metals in a mixed acid solution were tested. The minimum amount of an individual metal required for separation depended on the sensitivity of the subsequent detection method, *i.e.*, 5 *μg* for platinum, rhodium, iridium, and gold, and 3 *μg* for palladium. The maximum amount that can be separated depends first, on the solubility of the individual metal in a given amount of sample solution, and secondly on the width of the band occupied by that metal on the column.

Up to 3 mg of rhodium can be separated on a column 30 cm in length from milligram amounts of palladium, platinum, iridium and gold. The amount of palladium that can be separated from platinum depends on the band width of the latter. With increasing amounts of platinum, the retention time decreases, *i.e.*, the elution peak shifts towards that of the palladium. However, 1 mg of palladium can be separated from 5 mg of platinum. The amounts of iridium and platinum that have

TABLE IV.—THE RECOVERY OF GOLD

Gold added μg	Gold recovered* μg	Deviation μg
25	25	±1·5
50	50	±1·5
74	75	±1·5
100	105	+7·0 −3·0

* Average of four results

TABLE V.—THE EFFECT OF VARYING AMOUNTS OF IRIDIUM AND PLATINUM

1000 μg of Pt present		20 μg of Ir present	
Ir added μg	Ir recovered μg	Pt added μg	Pt recovered μg
5	6(±1·0)	200	195
10	10(±1·0)	400	370
25	24(±1·5)	500	480
50	46(±2·0)	1000	988(±20)
75	74(±1·0)		
100	95(±1·5)		

been tested under reducing conditions in the presence of 20 mg of sodium sulphite are shown in Table V. The recoveries are generally satisfactory when considered in relation to the errors associated with the methods of determination.

Relatively large amounts of gold (up to 20 mg/g of TBP-treated Porasil C) can be separated from all the other metals tested when these are eluted with 0·1*M* hydrochloric acid.

The effect of other variables

When the total amount of noble metals does not exceed 1500 μg, the amount of solution that can be applied to the column is not critical. However, in the separation of unknown amounts of noble metals, a volume not larger than 2 ml was maintained so that the peak-width for the metals to be separated would not be affected.

The presence of hydrochloric acid in the original solution was found to be necessary to ensure the dissolution of the combined noble-metal salts in 4*M* sulphuric acid. However, hydrochloric acid concentrations from 1 to 5*M* in the total amount of solution did not affect the course of separation, and the concentration was conveniently maintained at 2·5*M* in all experiments.

An initial flow-rate of 1 ml/min was maintained, but, since the flow-rate of the eluate was found not to be critical in stepwise elution, separations were done at the maximum speed for the column (approximately 2·5 ml/min).

Although the life span of a column used for the separation of noble metals under oxidizing conditions has not been thoroughly tested, columns have been used for fifteen successive separations without any deterioration. Columns for the separation of iridium from platinum under reducing conditions have been used ten times in succession.

Recommended procedure

The method[21] derived from this experimental work is summarized in Fig. 6. It should be observed that the sample solution is free from nitric acid and that the columns are preconditioned with the first acid solution to be used. Gold present on the column used for the separation of rhodium and palladium does not interfere with subsequent separations unless it accumulates to such an extent that the capacity of the column bed is considerably reduced. On a 3-cm column, to avoid incomplete recovery of the gold, owing to reduction, the gold must be extracted as quickly as possible with methyl isobutyl ketone (MIBK).

Approximately 12 hr are needed for all the procedures, including the quantitative determination of the individual noble metals. Exhausted columns can be reconditioned by removal of the organic phase with carbon tetrachloride and fresh treatment with TBP.

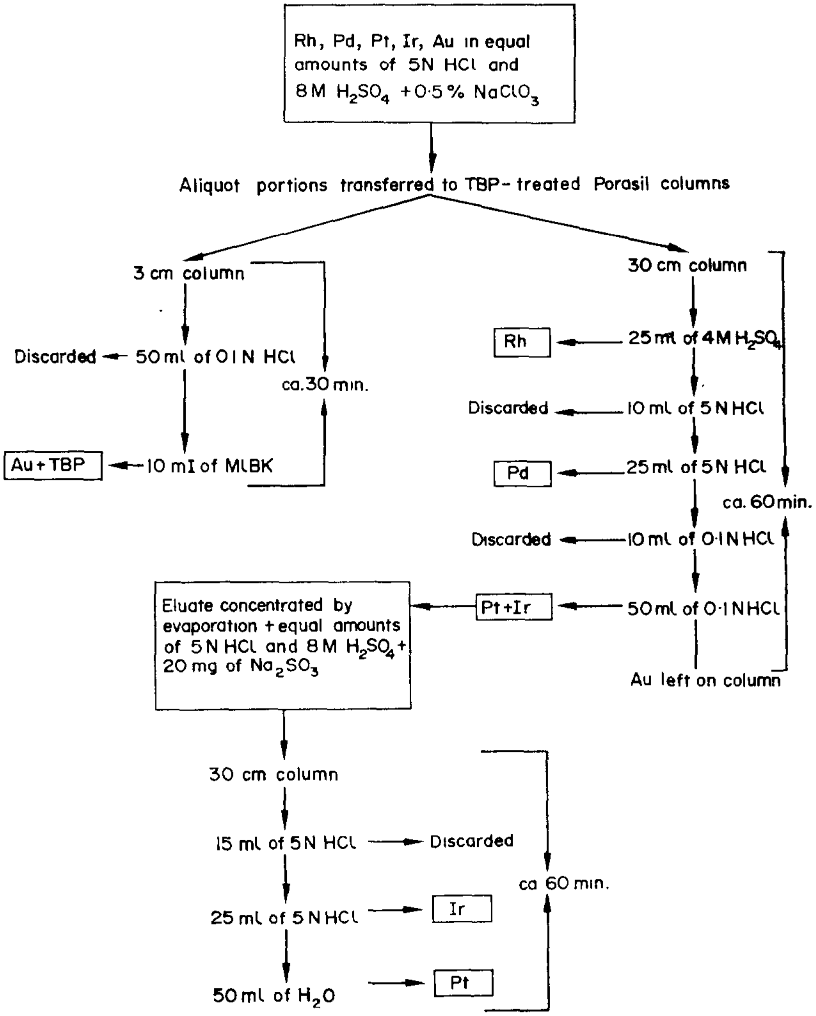


FIG. 6.—Separation of non-volatile noble metals by reversed-phase extraction chromatography.

Application of the method to ore samples

Since the results on synthetic solutions were satisfactory, the separation procedure was applied to the analysis of ore samples. Prills obtained from the fire assay of ores by the lead-collection procedure were dissolved in *aqua regia* or by chlorination in a sealed tube.[21]

Prills that were dissolved in *aqua regia* under atmospheric pressure were gently heated on a hot-plate. The solutions were then evaporated and the residues repeatedly treated with concentrated hydrochloric acid, being evaporated to a moist state after each addition of acid. After final evaporation to a moist state and the addition of 0·5 ml of 5*M* hydrochloric acid, 0·1 ml of a 5% solution of sodium chlorate, and 0·5 ml of 8*M* sulphuric acid, the solutions were ready for chromatographic separation.

Prills that were not readily dissolved under atmospheric pressure were transferred to glass tubes and, after the addition of 2 ml of concentrated hydrochloric acid and 6 drops of fuming nitric acid, the sealed tubes in a steel jacket were heated in an oven to 275° and were kept at this temperature overnight. After being cooled, the solutions were evaporated and from then on treated as described for the dissolution of prills with *aqua regia*. The total amount of sample solution or, when gold was determined in addition to the platinum-group metals, an aliquot portion of the suitably diluted sample solution, was transferred to the column, and the noble metals were separated and determined as described.

The results obtained for different sets of prills of a typical sample of Merensky Reef ore are shown in Table VI, together with comparative results from atomic-absorption spectroscopy. It should be borne in mind that the collection technique used for obtaining the prills is subject to errors and that the RPEC results are therefore not strictly comparable with the atomic-absorption results. Nevertheless, the agreement for platinum, rhodium and gold and, to a lesser extent, for palladium, is very satisfactory.

TABLE VI.—THE DETERMINATION OF NOBLE METALS IN PRILLS

Set of prills no.	Method of dissolution	Pt *ppm*	Pd *ppm*	Rh *ppm*	Ir *ppm*	Au *ppm*
1	Chlorination procedure	5·40	0·79	0·40	0·08	0·20
2		5·18	0·77	0·36	0·12	0·19
3		5·50	0·73	0·48	0·08	0·21
4		5·31	0·80	0·36	†	0·21
Average		5·35	0·77	0·40	0·10	0·20
Average of 6 results by direct *A.A. measurement		5·38	0·89	0·37	†	0·20
5	*Aqua regia*	5·36	0·85	0·35	†	†
6		5·12	0·79	0·28	†	0·20
7		5·20	0·86	0·35	†	†
8		5·50	0·75	0·34	0·08	†
Average		5·30	0·81	0·33	†	†
Average of 6 results by direct *A.A. measurement		5·23	0·91	0·35	†	0·20

* Atomic absorption
† not determined

CONCLUSIONS

Rhodium and palladium can be separated from each other and from the other non-volatile noble metals on a TBP-treated Porasil C column by stepwise elution with $4M$ sulphuric acid and $5N$ hydrochloric acid. Platinum and iridium are eluted together with $0.1M$ hydrochloric acid and separated on a second column under reducing conditions. Gold is collected on a third column, from which it is extracted with MIBK.

Noble metals in widely varying ratios have been separated. The analyses of a sample of ore from the Merensky Reef gave results that compare favourably with those obtained by atomic-absorption spectrometry.

Because of the success of the separation for non-volatile noble metals and because the column can be regenerated, the process could be considered for industrial use.

Acknowledgement—The authors wish to thank Mrs. M. Ewen and Mrs. A. Gereghty for competent technical assistance and the Director of the National Institute for Metallurgy for permission to publish this paper.

Zusammenfassung—Das Verfahren beruht auf der Verwendung von an Porasil C adsorbiertem Tri-n-butylphosphat (TBP) und die stufenweise Elution mit Schwefelsäure und Salzsäure. Die Verteilungskoeffizienten der beiden Systeme (TBP und Salzsäure sowie TBP und Schwefelsäure) und ihre Elutionseigenschaften wurden untersucht. Ein Verfahren wird beschrieben, das man zur Analyse von Reguli aus der Schmelzaufbereitung platinführender Erze verwenden kann.

Résumé—La technique comprend l'emploi de tri-*n*-butyl phosphate (TBP) adsorbé sur Porasil C et l'élution graduelle à l'acide sulfurique et à l'acide chlorhydrique. On a étudié les coefficients de partage pour les deux systèmes (TBP et acide chlorhydrique et TBP et acide sulfurique) et les caractéristiques d'élution. On décrit une technique applicable à l'analyse des boutons obtenus dans l'essai par voie sèche de minerais contenant du platine.

REFERENCES

1. J. Korkisch and H. Klakl, *Talanta*, 1968, **15**, 339.
2. L. N. Moskvin and B. K. Preobrazhenskii, *Radiokhimiya*, 1964, **6**, 237.
3. E. Blasius and D. Rexin, *Z. Anal. Chem.*, 1961, **179**, 105.
4. J. G. Sen Gupta and F. E. Beamish, *Am. Minerologist*, 1963, **18**, 379.
5. D. B. Rees-Evans, W. Ryan and R. A. Wells, *Analyst*, 1958, **83**, 321.
6. R. Fournier, *Rev. Met. (Paris)*, 1955, **52**, 596.
7. N. F. Kember and R. A. Wells, *Analyst*, 1955, **80**, 735.
8. G. S. James, *S. African Ind. Chemist*, 1961, **15**, 62.
9. C. Pohlandt and T. W. Steele, *Johannesburg, National Institute for Metallurgy, Rept* No. 1003 (3rd July 1970).
10. H. Eschrich and W. Drent, *Bibliography on Applications of Reversed Phase Partition Chromatography to Inorganic Chemistry and Analysis*, Eurochemic, Mol(Belgium), ETR 211.
11. E. Cerrai and G. Ghersini, *Advances in Chromatography, Vol. 9*, Dekker, New York, 1970.
12. L. S. Bark, G. Duncan and R. J. T. Graham, *Analyst*, 1967, **92**, 347.
13. L. S. Bark and D. Brandon, *Talanta*, 1969, **16**, 497.
14. F. W. O'Laughlin and C. V. Banks, *U.S. At. Energy Comm. Rept.*, JS-737, May 1963.
15. M. P. Volynets, A. N. Ermakov and L. P. Nikitina, *J. Anal. Chem. USSR*, 1970, **25**, 247.
16. M. A. Khattak and R. J. Magee, *Anal. Chim. Acta*, 1969, **54**, 297.
17. G. H. Ayres and W. T. Bolleter, *Anal. Chem.*, 1957, **29**, 72.
18. D. J. Pietrzyk, *Talanta*, 1969, **16**, 169.
19. T. Ishimori, *Data of Inorganic Solvent Extraction (1) and (3)*, Japan, JAERI, 1047 (1963) and JAERI, 1106 (1966).
20. I. Fidelis, R. Gwodz and S. Siekierski, *Nukleonika*, 1963, **8**, 327.
21. C. Pohlandt, M. Ewen and A. Gereghty, *Johannesburg National Institute for Metallurgy, Rept.* No. 994 (24th February 1971).

Talanta, 1972, Vol. 19, pp. 851 to 856. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF TRACE AMOUNTS OF URANIUM IN SILICATE MINERALS BY THE FISSION TRACK TECHNIQUE

HIDEKI MATSUDA, YUTAKA TSUTSUI, SHIGENORI NAKANO and SHUNJI UMEMOTO
Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Fukuoka, Japan

(*Received* 30 *August* 1971. *Accepted* 14 *October* 1971)

Summary—The fission track technique has been applied to the determination of uranium on Dowex 1 × 8 after chemical separation from silicates. Standard rock and several stone meteorite samples were treated by this method and satisfactory results were obtained. The procedure is applicable to natural waters.

IN RECENT YEARS, application of the fission track technique has been developed in the field of nuclear physics, neutron dosimetry, cosmochemical studies and geochronology.[1] Fission tracks are produced in several insulating solid materials such as micas, glasses and plastics. So far, the application of this technique to uranium determination has been carried out by few investigators. Hashimoto[2] examined the sensitivities of detection for the actinide elements with neutron-induced fission tracks, and found that ^{235}U is the most sensitive of the nuclides examined and $6{\cdot}24 \times 10^{10}$ fission events are available from 1 μg of this isotope by thermal neutron irradiation of $4{\cdot}21 \times 10^{14}$ n/mm^2. However, ^{238}U and ^{232}Th also gave $3{\cdot}2 \times 10^7$ and $1{\cdot}75 \times 10^6$ fission events per μg. Fleischer[3] observed the uranium distribution in the silicate minerals of several stony meteorites by the fission track method and found a tremendous variation of uranium content within a small area. The uranium contents were determined by the mapping procedure and were found to be different from the previous values in a few cases. On the other hand, by neutron-activation analysis,[4] the present authors found a different distribution pattern, from chondrite to chondrite, of uranium in the silicate minerals of several stony meteorites. The uranium distribution of the Richardton chondrite showed an unexpected pattern, that is, only 20–30% of the uranium was found in the hydrochloric acid soluble fraction. As about 70% was found in the same fraction of the other meteorites, a cross-check by the alternative method is desirable.

Hashimoto *et al.*[5] determined concentrations of a few ppm of uranium by a fission track method. In their experiment, a mica detector was attached to the powdered standard rock and the result showed relatively good agreement with the previous data. Bertine *et al.*[6] also determined the uranium content of homogenized powdered samples of sedimentary rocks, utilizing a digital discharge counter instead of visual counting.

All determinations of uranium by the fission track method were carried out without chemical separation of thorium and were performed on samples containing a few ppm of uranium (with the exception of Fleischer's[3]). However, since these fission track methods have relatively high back-grounds and low sensitivities for less than 1 ppm of uranium and errors arise from fission tracks produced from ^{238}U and ^{232}Th, these methods are not suitable for the determination of trace amounts (of the order of ppb) of uranium in silicate minerals or in samples of unknown thorium content.

The present authors avoided these difficulties by a simple chemical treatment followed by anion-exchange separation applied to the several standard rocks and stony meteorites.

EXPERIMENTAL

On the assumption that the fission tracks produced in micas attached to the fine grains of resin absorbing uranium are homogeneously distributed, the irradiation samples were prepared and bombarded with thermal neutrons.

The distribution coefficient of the uranyl ion between strong-base anion-exchange resins and 8*M* hydrochloric acid is about 10^3 and that for iron(III) is also fairly large, but thorium(IV) is not adsorbed on the resin under the same conditions.[7] Since iron is one of the main constituents of silicate minerals, a relatively large amount of iron will be adsorbed on the resin along with uranium unless iron is removed in advance.

Silicate samples were dissolved with hydrofluoric acid and perchloric acid in a platinum dish. The solution was made 8*M* in hydrochloric acid, and most of the iron was removed by extraction with di-isopropyl ether. Thorium was removed by anion-exchange. The uranium adsorbed on the resin column was eluted and purified. The procedure is given in Fig. 1. The purified uranium was dissolved in 2 ml of 8*M* hydrochloric acid, then 100 mg of pulverized anion-exchange resin (Dowex 1 × 8) were added to this solution, and the mixture was allowed to stand for 12 hr with occasional stirring. The resin was filtered off, and transferred into the sample holder (Fig. 2).

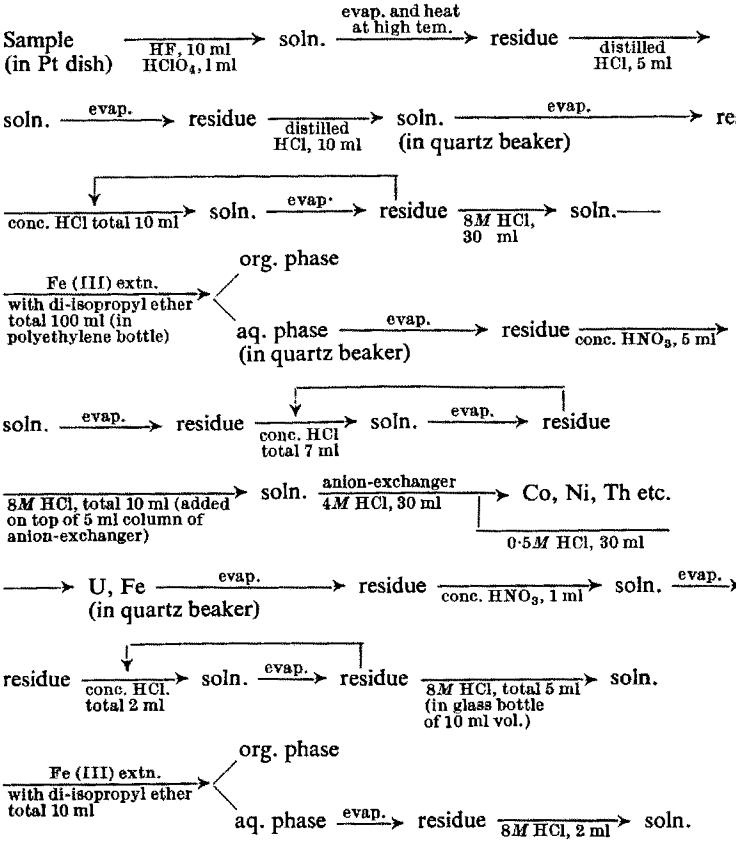


FIG. 1.—Flow-sheet of the chemical procedure used for silicate minerals and for blank test.

The sample holder and its support are square sheets of Perspex 1 mm and 5 mm in thickness having 4 mm diameter holes. A mica detector is attached to the bottom of the holder, and the support is fixed to the top of the holder, and the assembly taped together.

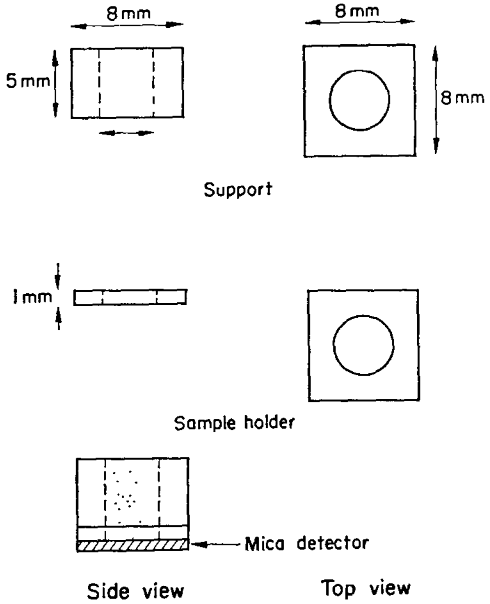


FIG. 2.—Side and top views of sample holder and support.

The resin is placed in the hole, and compacted by centrifugation. The support and excess of resin are removed and the top of the holder and the mica detector are covered with thin Perspex sheets and taped together.

An aliquot of a standard uranium solution was evaporated to dryness in a quartz beaker, and 2 ml of 8*M* hydrochloric acid were added and the solution was treated in the same way as the samples.

In order to determine the uranium content of the reagents, aliquots of demineralized water, distilled water, hydrochloric acid, distilled hydrochloric acid, nitric acid, hydrofluoric acid and di-isopropyl ether were weighed out on a Perspex plate and evaporated to dryness under an infrared lamp. A mica detector was taped to the plate.

The samples (except W-1), the reference standards(II) and the blank were placed together in a capsule and irradiated with thermal neutrons in a pneumatic tube of the KUR reactor of the Research Reactor Institute at Kyoto University. The total neutron flux was $8\cdot4 \times 10^{14}$ n/mm^2. The sample W-1, the reference standards(I), and the reagent blanks were irradiated in a different run in the same tube and the total neutron flux was $3\cdot36 \times 10^{14}$ n/mm^2.

A few days after the irradiation, all mica detectors were etched with 46% hydrofluoric acid at 20° for 30 min. The etch pits developed in each detector were counted under an optical microscope.

In each detector the density of the etch pits was measured in five different arbitrarily chosen areas and the density value was taken as the average together with the 95% confidence limits. In the reagent detectors all the etch pits were counted.

RESULTS AND DISCUSSION

The reference standards gave fairly linear working curves. The limit of detection is about 1 ng of uranium in the original sample, and the determination limit 2–3 ng.

The uranium contents of the various silicate samples were determined by using the working curves, and the results are shown in Table I. The result was obtained after subtraction of the blank including that due to the mica detectors. The Richardton meteorite samples were supplied by Honda,[20] who separated this meteorite into two fractions, white powder and black grains, the amounts in both fractions being similar. Each of these two fractions was further divided into a hydrochloric acid soluble and a hydrochloric acid insoluble fraction (5*M* hydrochloric acid). The former is designated as HCl and the latter as HF in Table I. The overall uranium

TABLE I.—OBSERVED URANIUM CONTENTS OF STANDARD ROCKS AND STONY METEORITES

	Sample	Sample weight *g*	Observed track density, *number/area**	Net track density, *number/area**	Uranium in samples *ng*	Uranium content *ppB*	Previous data *ppB*
	Blank		1·6 ± 1·0				
Standard rock	DTS-1	0·6881	15·8 ± 1·1	14·2 ± 1·5	2·6 ± 0·2	3·8 ± 0·4	3·2(8), 4(9), 3(10), 3·7(11)
	PCC-1	0·6176	12·8 ± 2·8	11·2 ± 2·9	2·1 ± 0·5	3·4 ± 0·9	4·0(8), 5(9),(10), 4·8(11),
	G-1	0·0100	173 ± 8·6	173 ± 8·6†	32·8 ± 1·6	3280 ± 160	3700 ± 500(12), 2800(13), 4420(9),
	W-1	0·0446	33·0 ± 2·2	33·0 ± 2·2§	25·2 ± 1·0	542 ± 36	480(12), 620(9), 460(14),
Stony meteorite	*Bruderheim*	0·5179	30·6 ± 3·0	29·0 ± 3·1	5·4 ± 0·5	10·5 ± 1·1	20(3), 11, 18, 17(15), 10·9, 13·4(16), 10·6, 10·7, 10·0(4),
	Allende	0·5025	43·0 ± 3·4	41·4 ± 3·5	7·8 ± 0·6	15·5 ± 1·3	16·3, 16·0(17),
	Richardton (white powder)	0·5842					
	HCl		14·0 ± 3·2	12·4 ± 3·3	2·3 ± 0·6	4·0 ± 1·0	7·3, 10·6(4),
	HF		15·4 ± 1·8	13·8 ± 2·0	2·6 ± 0·3	4·4 ± 0·6	13·2(15), 10·7(18), 11·3, 13·0(19),
	(black grain)	0·3744					
	HCl		8·2 ± 1·6	6·6 ± 1·8	1·2 ± 0·3	3·3 ± 0·9	
	HF		20·0 ± 2·3	18·4 ± 2·5	3·4 ± 0·4	9·2 ± 1·2	

* 0·159 mm^2.

† The blank is too small to subtract.

§ The blank was not measured.

content of the Richardton sample was calculated as the weighted mean of its content in each fraction.

Most of the uranium contents shown in Table I are in between the various values previously reported, but Allende and PCC-1 are slightly lower than the lowest. The blank value shown in Table I is thought to originate from the reagents and contamination.

The uranium contents of the reagents used are tabulated in Table II. The amount of uranium in the reagent samples is obtained by using the equation

TABLE II.—URANIUM CONTENTS OF REAGENTS USED

Sample	Sample wt, *mg*	Total observed tracks	Net number of tracks	Uranium content, *ppt**
Blank mica 1		30		
Blank mica 2		29		
Demineralized H_2O	19·2	35	5 ± 8	0·7 ± 1·2
Distilled H_2O	27·1	55	25 ± 9	2·6 ± 0·9
Conc. HCl	51·6	34	4 ± 8	0·2 ± 0·4
Distilled HCl	$38{\cdot}0_8$	66	36 ± 10	2·7 ± 0·7
Conc. HNO_3	$34{\cdot}5_6$	23	−7 ± 7	−0·6 ± 0·6
Conc. HF	$26{\cdot}9_7$	37	7 ± 8	0·7 ± 0·8
Di-isopropyl ether	7	24	−6 ± 7	−2·5 ± 4
Conc. NH_3 soln.†	$28{\cdot}0_7$	180	150 ± 14	15·2 ± 1·1

* Parts in 10^{12}
† Only for reference

$$M = (T/f\sigma) \times (235/A) \times (1/I) = 2{\cdot}84 \times 10^{-15}T$$

where M is the amount of uranium in the samples (in g), T the number of tracks observed in the samples, f the neutron flux ($3{\cdot}36 \times 10^{14}$ n/mm^2), σ the fission cross-section (577 barn),[21] A Avogadro's number, and I the isotopic fraction of ^{235}U (0·72%).[21] Distilled water was prepared from demineralized water and distilled hydrochloric acid from concentrated hydrochloric acid and demineralized water, and the vessel used was made of quartz. The result suggests that the distillation process caused uranium contamination. From the calculation of the amount of uranium introduced from the reagents during the chemical treatment and from the preliminary experiment, the resin blank is negligibly small.

The result for the Richardton meteorite is shown in Table III together with the previous data of Bruderheim, Abee, St. Marks, and Richardton.[4] The uranium content of the hydrochloric acid soluble fractions is higher than that of the insoluble

TABLE III.—URANIUM CONTENTS OF THE HCl AND HF FRACTION OF STONY METEORITES[4]

Fraction	Bruderheim *ppB* 1	Bruderheim *ppB* 2	Abee *ppB*	St. Marks *ppB*	Richardton *ppB* 1	Richardton *ppB* 2	Richardton *ppB* this work*
HCl	7·7	7·0	14·6	18·0	2·0	2·2	3·7
HF	2·9	3·7	—	5·4	5·3	8·4	6·8

* These values are the weighted mean of the uranium content of white powders and black grains.

fractions in the results of Bruderheim, Abee and St. Marks, but not in those of Richardton. With a slight modification this procedure is also applicable to the determination of the uranium content of natural waters.

Acknowledgement—The authors wish to thank Dr. Honda of the University of Tokyo for the generous gift of the Bruderheim and the separated and whole Richardton samples, Dr. Y. Matsui of Okayama University for G-1, W-1 and DTS-1, Dr. K. Ishibashi of Kyushu University for G-1, W-1, PCC-1 and DTS-1 and Dr. R. S. Clark of the Smithsonian Institute for Allende. Thanks are also due to Drs. S. Iwata and Y. Kiso and the staff of Kyoto University for the irradiation facilities.

Zusammenfassung—Das Spaltspurverfahren wurde auf die Bestimmung von Uran an Dowex 1 × 8 nach chemischer Abtrennung von Silikaten angewandt. Standard-Gesteinsproben und Proben von mehreren Gesteins-Meteoriten wurden nach diesem Verfahren behandelt und es wurden befriedigende Ergebnisse erhalten. Die Vorschrift läßt sich auf natürliche Wässer anwenden.

Résumé—On a appliqué la méthode de trajectoire de fission au dosage de l'uranium sur Dowex 1 × 8 aprés séparation chimique des silicates. On a traité par cette méthode une roche étalon et plusieurs échantillons de pierres météoritiques, et l'on a obtenu des résultats satisfaisants. La technique est applicable aux eaux naturelles.

REFERENCES

1. R. L. Fleischer, P. B. Price and R. M. Walker, *Science*, 1965, **149**, 383.
2. T. Hashimoto, *Bunseki Kagaku*, 1970, **19**, 508.
3. R. L. Fleischer, *Geochim. Cosmochim. Acta*, 1968, **32**, 989.
4. H. Matsuda, M. Honda and M. Shima, private communication.
5. T. Hashimoto, S. Hayashi and S. Iwata, *Bunseki Kagaku*, 1970, **19**, 1538.
6. K. K. Bertine, L. H. Chan and K. K. Turekian, *Geochim. Cosmochim. Acta*, 1970, **34**, 641.
7. K. A. Kraus and F. Nelson, *Proc. Intern. Conf. Peaceful Uses of Atomic Energy, Geneva*, 1955, 1956, **7**, 113.
8. J. W. Morgan and K. S. Heier, *Earth Planet. Sci. Lett.*, 1966, **1**, 158.
9 N. H. Gale, *Symp. Radioactive Dating and Methods of Low-level Counting*, 1967, 431, IAEA, Vienna.
10. E. I. Hamilton, *Earth Planet. Sci. Lett.*, 1966, **1**, 317.
11. F. J. Flanagan, *Geochim. Cosmochim. Acta*, 1969, **33**, 81.
12. L. H. Ahrens, R. D. Cherry and A. J. Erlank, *ibid.*, 1967, **31**, 2379.
13. A. Alian and R. Parthasarathy, *Anal. Chim. Acta*, 1966, **35**, 69.
14. G. D. Nicholls, A. L. Graham, E. Williams and M. Wood, *Anal. Chem.*, 1967, **39**, 584.
15. G. G. Goles and E. Anders, *Geochim. Cosmochim. Acta*, 1962, **26**, 723.
16. R. S. Clark, M. W. Rowe, R. Ganapathy and P. K. Kuroda, *ibid.*, 1967, **31**, 1605.
17. E. L. Fireman, J. DeFelice and E. Norton, *ibid.*, 1970, **34**, 873.
18. H. Hamaguchi, G. W. Reed and A. Turkevich, *ibid.*, 1957, **12**, 337.
19. J. W. Morgan and J. F. Lovering, *Talanta*, 1968, **15**, 1079.
20. M. Honda, private communication.
21. C. M. Lenderer, J. M. Hollander and I. Perlman, *Table of Isotopes* (*6th Ed.*), Wiley, New York, 1967.

Talanta, 1972, Vol. 19, pp. 857 to 862. Pergamon Press. Printed in Northern Ireland

RAPID MASS-SPECTROMETRIC DETERMINATION OF BORON ISOTOPIC DISTRIBUTION IN BORON CARBIDE

JAMES E. REIN and ROBERT M. ABERNATHEY
University of California, Los Alamos Scientific Laboratory, Los Alamos,
New Mexico 87544, U.S.A.

(*Received* 24 *August* 1971. *Accepted* 24 *October* 1971)

Summary—Boron isotopic ratios are measured in boron carbide by thermionic ionization mass spectrometry with no prior chemical separation. A powder blend of boron carbide and sodium hydroxide is prepared, a small portion is transferred to a tantalum filament, the filament is heated to produce sodium borate, and the filament is transferred to the mass spectrometer where the $^{11}B/^{10}B$ ratio is measured, using the $Na_2BO_2^+$ ion. Variables investigated for their effect on preferential volatilization of ^{10}B include the sodium hydroxide–boron carbide ratio and the temperature and duration of filament heating. A series of boron carbide pellets containing natural boron, of the type proposed for the control rods of the Fast Flux Test Facility reactor, were analysed with an apparently unbiased result of 4·0560 for the $^{11}B/^{10}B$ ratio (standard deviation 0·0087). The pellets contained over 3% metal impurities typically found in this material. Time of analysis is 45 min per sample, with one analyst.

BORON CARBIDE is a commonly used material as a burnable poison in nuclear fuels and as a neutron absorber in nuclear reactor control rods. The ^{10}B isotope with a natural abundance of 19·8 atom % provides this property because of its thermal neutron cross-section of 3840 barn. The proposed material form for the control rods of the Fast Flux Test Facility under construction at Richland, Washington for the AEC's Fast Breeder Reactor programme is compressed 1·2-g pellets of boron carbide. The analytical method described in this paper for the determination of boron isotope ratios in this material should also be applicable to all boron carbide materials with ^{10}B isotopic abundances ranging from natural to high enrichment.

As discussed in the excellent monograph by Lerner,[1] most boron materials are analysed isotopically for boron isotope ratios with thermionic ionization mass spectrometers. The ion usually measured is $Na_2BO_2^+$ from a charge material of sodium tetraborate.[2] The general scheme used to obtain sodium tetraborate is to dissolve samples either by sodium carbonate fusion or acid reflux, separate the boron as boric acid by such techniques as distillation of the methyl ester or by cation-exchange removal of metal impurities, and neutralize the separated boric acid with sodium hydroxide to pH $9·2 \pm 0·2$. All these schemes are time-consuming, especially the dissolution of boron carbide samples, and involve many reagents and operations that are potential sources of boron contamination. The mass spectrometric technique of Spitzer and Sites[3] offers the means to analyse boron carbide directly with virtually no chemical operations. In their technique, a sample of boron metal or of a boron compound is added to a tantalum filament containing a small amount of sodium hydroxide, the filament is heated to approximately 750° to produce sodium borate

---

* This work was sponsored by the Fuels and Materials Branch of the Division of Reactor Development and Technology of the U.S. Atomic Energy Commission.

(presumed to be sodium tetraborate), which is mass spectrometrically analysed as the $Na_2BO_2^+$ ion spectrum.

Preliminary experimentation with the Spitzer and Sites technique confirmed production of the $Na_2BO_2^+$ spectrum; however, ion production was erratic and the scans were unstable. This inconsistency was presumed to be caused by the physical difficulty of obtaining reproducible ratios of sodium hydroxide and boron carbide on the filament. Reproducible ratios are considered necessary to obtain effective fusions and conversions into sodium borate. Their technique has been made the basis of an improved method of analysis that is based on first blending weighed amounts of pulverized boron carbide and pulverized sodium hydroxide, then fusing a small portion of the blend on a tantalum filament, followed by the mass spectrometric analysis. Shields and co-workers[4] found that preferential volatilization of ^{10}B from sodium tetraborate may occur, depending on the Na/B ratio and the temperature and duration of filament heating. These three variables were studied for the development of the method described in this report.

EXPERIMENTAL

Reagents

Boron carbide. Two batches of boron carbide were used in this study. Both contained natural boron. The first, a fine powder, was used for all experiments to evaluate effects of variables. The second, a batch of well-characterized pellets prepared by the Hanford Engineering Development Laboratory (Richland, Washington), was used to establish the precision of the method and the tolerance of the method for impurities.

Sodium hydroxide, pellets, analytical-reagent grade. Powder was prepared by a 1-min pulverization with a Mixer/Mill, using stainless-steel containers and balls. The powder was stored in a desiccator. Although the laboratory atmosphere had a relative humidity of 50%, no coalescence of the powder was experienced.

Apparatus

Mixer/Mill, No. 5100: Spex Industries, P.O. Box 798, Metuchen, N.J. 08840.

Plastic mixing containers and balls. Containers were 13-mm o.d. and 25 mm long, polystyrene, with polyethylene slip-on caps (Spex No. 3111). The balls were 9-mm diam, methacrylate (Spex No. 3112).

Mass spectrometer, thermionic ionization. AVCO Model No. 90001, 0·35 m radius, 90° sector.

Filaments. Tantalum and rhenium, 30-mil wide, 1·2-mil thick.

Filament heating apparatus. Capable of preheating filaments to about 800°.

General procedure

A quantity of pulverized sodium hydroxide (fresh from the desiccator) is weighed to ±1 mg into a plastic mixing container and 25 mg of B_4C are transferred to the container with minimum exposure of the contents to air moisture. (The amount of sodium hydroxide is dictated by the desired ratio of Na/B.) A plastic ball is added, the cap is placed on the container, and the contents are blended for 1 min on the Mixer/Mill. With a stainless-steel microspatula, a portion of the blend containing about 10 μg of boron is transferred to a V-grooved tantalum filament. The filament is gradually heated just to the point where the exothermic reaction of the sodium hydroxide with the filament occurs. (This reaction is characterized by a sudden brightening of the filament.) The filament with fused sample is transferred to the mass spectrometer and the spectrum is measured for the mass range 88–89 ($Na_2BO_2^+$). A Faraday cup detector is used and 9 spectra recorded after a stabilized ion-current is attained. The $^{11}B/^{10}B$ ratio is measured and converted into atom % abundances if desired. The ^{17}O correction to the $^{11}B/^{10}B$ ratio is 0·00075.

RESULTS AND DISCUSSIONS

In the comprehensive study by Shields and co-workers,[4] who used samples of boric acid reacted both with sodium hydroxide and sodium carbonate, the measured $^{11}B/^{10}B$ ratio was shown to depend on the Na/B ratio, the filament temperature and the residence time in the mass spectrometer. In all experiments, the $Na_2BO_2^+$ ion-beam intensity was maintained at 1–2 pA, and where possible the filament current was maintained within a narrow range to yield constant filament temperatures. With sodium hydroxide reacted samples, the greatest variation in $^{11}B/^{10}B$ ratio was caused by a varying Na/B ratio. At Na/B ratios of 1/2 and 1/1, the observed $^{11}B/^{10}B$ ratios were not significantly different nor did the ratios change much with filament heating time. At a higher ratio of 2/1, the $^{11}B/^{10}B$ ratio increased by as much as 1% as well as increasing further with filament heating time and temperature. At an Na/B ratio of 4/1, the $Na_2BO_2^+$ ion-current was suppressed so much that the filament current had to be increased considerably to obtain the $Na_2BO_2^+$ ion intensity of 1–2 pA. The consequent increased temperature caused isotopic fractionation and hence the observed increase in the $^{11}B/^{10}B$ ratio. Another significant finding was an aging phenomenon with sodium hydroxide-reacted boric acid samples. When these samples were stored for two weeks before mass analysis, the solutions with an Na/B ratio of 4/1 gave the desired 1–2 pA $Na_2BO_2^+$ ion-current at a filament current almost as low as that used for the 1/2 and 1/1 Na/B ratio samples, instead of at the higher filament current noted above.

In the method proposed in this paper, the sample preparation conditions are very different from those used by Shields *et al.* The most striking difference is that the sodium hydroxide fusion reaction with boron carbide is done on the filament. As the filament temperature is raised, the sodium hydroxide forms a melt, the mixture spreads over the filament, and then fuses when the temperature rises to the point where the tantalum reacts with the sodium hydroxide. At this point, the reaction becomes highly exothermic, the filament glows brightly and a very adherent deposit forms on the filament. Preliminary experiments showed that such filament preparations gave quickly attained and stable $Na_2BO_2^+$ ion intensities. With this very different method of sample preparation, blends of boron carbide and sodium hydroxide were prepared (as described under *General procedure*) with Na/B ratios varing from 1/4 to 4/1 and were analysed for the $^{11}B/^{10}B$ ratio, using the $Na_2BO_2^+$ ion. A scan was taken as soon as stable emission was attained at an ion intensity of 1–2 pA and a second scan was taken 15–30 min later at the same ion-intensity level with the filament current left on between scans. Filament temperatures were estimated for each scan from the filament currents, based on an optical pyrometer calibration.

The results (Table I) show complete randomness with no trend of an increasing $^{11}B/^{10}B$ ratio with either an increasing Na/B ratio or filament heating time. Also, there is no trend of an increasing $^{11}B/^{10}B$ ratio with increasing filament current. It appears that the boron carbide is mainly converted into sodium borate at the time of the exothermic reaction of the sodium hydroxide with the tantalum filament. Because of these simultaneous reactions and the formation of a tightly adherent deposit, the amount of sodium hydroxide in excess of that used to form borate is reduced and decreases the Na/B ratio effect on the $^{11}B/^{10}B$ ratio. It seems unlikely that boron isotope fractionation would occur in the short time that the high-temperature reaction occurs. Indirect evidence to substantiate this belief is that the grand average $^{11}B/^{10}B$ result of 4·0465 (Table I) corresponds to 19·81% ^{10}B, which is only slightly greater than the generally accepted value of 19·78% for natural boron.

As a further test of the effect of filament heating time on the measured $^{11}B/^{10}B$ ratio, filament with a 1/1 Na/B ratio was scanned for a continuous period of 5·5 hr.

TABLE I.—EFFECT OF Na/B RATIO, FILAMENT HEATING TIME AND FILAMENT TEMPERATURE ON THE MEASURED ^{11}B/^{10}B RATIO*

Na/B ratio	Number of samples	First scan ^{11}B/^{10}B	First scan Fil. temp	Second scan ^{11}B/^{10}B	Second scan Fil. temp
1/4	3	4·021	>1000	4·030	>1000
		4·064	~700	4·044	740
		4·070	~720	4·046	770
	Average	4·052 ± 0·015†		4·040 ± 0·005†	
1/2	6	4·047	~700	4·035	~700
		4·021	830	4·026	870
		4·019	740	4·033	740
		4·050	740	4·035	740
		4·052	<700	4·037	<700
		4·035	~700	4·043	740
	Average	4·037 ± 0·006†		4·035 ± 0·002†	
1/1	3	4·049	~700	4·028	~700
		4·041	<700	4·035	<700
		4·041	<700	4·051	<700
	Average	4·044 ± 0·003†		4·038 ± 0·007†	
2/1	3	4·049	740	4·064	790
		4·056	790	‡	–
		4·038	~700	4·059	740
	Average	4·048 ± 0·005†		4·062 ± 0·003†	
4/1	3	4·038	740	4·078	740
		4·044	740	4·042	740
		4·063	>700	4·065	740
	Average	4·048 ± 0·008†		4·062 ± 0·010†	
	Grand average	4·046		4·047	

* Ratio corrected for ^{17}O.

† Standard deviation.

‡ Ion emission too unsteady to permit data collection.

The filament temperature was essentially constant at 700° for most of the time, increasing to about 750° at the end of the period. The results summarized in Table II show no significant trend of an increase in the ^{11}B/^{10}B ratio with time.

TABLE II.—STABILITY OF ^{11}B/^{10}B RATIO WITH FILAMENT HEATING TIME WITH A SAMPLE LOADING OF FUSED BORON CARBIDE IN SODIUM HYDROXIDE WITH A 1/1 Na/B RATIO

Time of scan, after sample insertion	Measured ^{11}B/^{10}B ratio
15 min	4·041
30 min	4·051
1·5 hr	4·043
2·5 hr	4·046
3·5 hr	4·049
4·5 hr	4·055
5·5 hr	4·052

Based on observations made in the previous experiments, the use of a 1/1 Na/B ratio is recommended for routine use. Steady $Na_2BO_2^+$ ion emission is obtained within a few minutes after pump-down (10^{-7} mbar in the source) and remains so for hours. With Na/B ratios of 1/2 and 2/1, however, the time needed to attain steady ion emission can be as long as 30 min. At 1/4 and 4/1 ratios, the obtaining of steady ion emission requires undue patience. Also at a 4/1 ratio, filament burn-outs are common, and undoubtedly caused by corrosive degradation of the filament. With a 1/1 Na/B ratio, the weight of sodium hydroxide to use in the procedure is 72 mg for the recommended 25-mg boron carbide sample.

Upon first consideration, the substitution of rhenium for tantalum filaments seemed logical. Because of the low reactivity of rhenium with sodium hydroxide, the likelihood of filament burn-out diminishes. Also with little reaction taking place, the Na/B ratio of the mixture placed on the filament is not affected. A series of six filament loadings of boron carbide–sodium hydroxide blends was prepared at a Na/B ratio of 1/1. In all cases, the instrument residence time to reach stable ion emission was greater than 30 min compared to less than 10 min for tantalum filaments. In two cases, the ion emission was still erratic after 60 min. This finding is indirect evidence that the exothermic reaction of sodium hydroxide with tantalum gives a sodium borate deposit that uniquely produces stable $Na_2BO_2^+$ ion intensities. Shields *et al.*[4] reported that tantalum filaments gave more stable ion intensities than rhenium. Also in agreement with Shields, we find that tantalum filaments do not require prebaking and that at the low temperature used for ionization of sodium borate, no strontium impurity is volatilized from the filament to cause high bias in the 88 mass peak.

The only potentially significant source of boron contamination in the proposed method is the sodium hydroxide, the only reagent used. The plastic mixing containers and balls are sufficiently inexpensive to be thrown away. Natural boron contamination in the sodium hydroxide is effectively measured by using the NBS ^{10}B-enriched boric acid (SRM952). The sodium hydroxide used in this investigation (see *Reagents*) was tested by preparing a solution in distilled water in a plastic container, mixing this solution with a solution of the NBS 952 boric acid to form a Na/B ratio of 1/1, and applying mass spectrometric analysis. The level of boron found was less than 70 μg of boron per gram of sodium hydroxide. In the proposed procedure using a 25-mg boron carbide sample and 72 mg of sodium hydroxide (Na/B ratio of 1/1), this level is equivalent to less than 1 atom of natural boron contamination per 4000 atoms of sample boron.

The method was used to analyse a series of 12 boron carbide samples selected randomly from one batch of pellets. The pellets were pulverized by hammer blows in a stainless-steel mortar and the powder fractions passing through a 100-mesh sieve were used as the samples. The general procedure was used with 25 mg of boron carbide and 72 mg of sodium hydroxide (Na/B ratio of 1/1) and V-grooved tantalum filaments. The average result for the $^{11}B/^{10}B$ ratio, corrected for ^{17}O, for the 12 samples was 4·0506 with a standard deviation of 0·0087 for a single sample analysis. The ^{10}B isotopic abundance corresponding to the average $^{11}B/^{10}B$ ratio result of 4·0506 is 19·80%.

The impurity contents of the pellets are given in Table III. There is no apparent adverse effect from these impurities, which in this method are not separated from the boron, on the $Na_2BO_2^+$ ionization process.

The 12 samples were analysed in a total elapsed time of 9 hr by one analyst, exclusive of the initial pellet pulverization.

Future studies being considered are the substitution of caesium hydroxide for

TABLE III.—IMPURITY CONTENTS OF BORON CARBIDE PELLETS.

Element	$\mu g/g$	Element	$\mu g/g$
Al	5000	Mn	600
Bi	<25	Ni	400
Ca	1500	Si	4000
Co	<50	Sn	<10
Cr	300	Ti	1500
Cu	20	V	1000
Fe	15000	Zr	1000
Mg	<20		

sodium hydroxide and the applicability of the method to other boron materials. The higher mass of $Cs_2BO_2^+$ should decrease any preferential volatilization effect and would also have the advantage of a smaller mass discrimination correction for those laboratories that prefer to use electron multiplier detectors. Other boron materials include the metal, the oxide, and boric acid.

Zusammenfassung—Bor-Isotopenverhältnisse in Borcarbid werden durch Massenspektrometrie mit thermischer Ionisierung ohne vorausgehende chemische Abtrennung gemessen. Ein Pulvergemisch von Borcarbid und Natriumhydroxid wird hergestellt und eine kleine Portion davon auf einen Tantalfaden gebracht. Der Faden wird geheizt, wobei sich Natriumborat bildet, und dann ins Massenspektrometer gebracht, wobei am $Na_2BO_2^+$-Ion das Verhältnis $^{11}B/^{10}B$ gemessen wird. Auf ihren Einfluß auf die bevorzugte Verflüchtigung von ^{10}B wurden folgende Variable geprüft: das Verhältnis Natriumhydroxid zu Borcarbid und Temperatur und Dauer der Erhitzung des Fadens. Eine Reihe von natürliches Bor enthaltenden Borcarbidpreßlingen vom für die Kontrollstäbe des Fast Flux Test Facility-Reaktors vorgeschlagenen Typ wurden analysiert; das offenbar von systematischen Fehlern freie Ergebnis betrug 4,0560 für das $^{11}B/^{10}B$-Verhältnis (Standardabweichung 0,0087). Die Preßlinge enthielten über 3% metallische Verunreinigungen, wir sie üblicherweise in diesem Material gefunden werden. Die Analysenzeit beträgt für einen Analytiker 45 min je Probe.

Résumé—On mesure les rapports isotopiques du bore dans le carbure de bore par spectrométrie de masse à ionisation thermoionique sans séparation chimique préalable. On prépare un mélange en poudre de carbure de bore et de soude, en transfère une petite portion sur un filament de tantale, le filament est chauffé pour produire du borate de sodium, et le filament est transféré dans le spectromètre de masse où l'on mesure le rapport $^{11}B/^{10}B$ en utilisant l'ion $Na_2BO_2^+$. Les variables étudiées quant à leur influence sur la volotalisation préférentielle de ^{10}B comprennent le rapport soudecarbure de bore et la température et la durée de chauffage du filament. On a analysé une série de pastilles de carbure de bore contenant du bore naturel, du type proposé pour les baguettes de contrôle du réacteur Fast Flux Test Facility, avec un résultat apparemment impartial de 4,0560 pour le rapport $^{11}B/^{10}B$ (écart type 0,0087). Les pastilles contenaient plus de 3% d'impuretés métalliques typiquement trouvés dans cette matière. Le temps d'analyse est de 45 mn par échantillon, avec un analyste.

REFERENCES

1. M. W. Lerner, *The Analysis of Elemental Boron*, *U.S. At. Energy Comm. Rept.* TID-25190, Section 5-3, 1970.
2. G. H. Palmer, in *Advances in Mass Spectrometry*, ed. S. D. Waldron, Pergamon, London, 1959.
3. E. J. Spitzer and J. R. Sites, *U.S. At. Energy Comm. Rept.*, ORNL-3528, p. 12, 1963.
4. E. J. Catanzaro, C. E. Champion, E. L. Garner, G. Marinenko, K. M. Sappenfield, and W. R. Shields, *Natl. Bur. Stds. Spec. Publ.* 260-17, 1970.

Talanta, 1972, Vol. 19, pp. 863 to 869. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF NIOBIUM IN ROCKS, ORES AND ALLOYS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

JOHN HUSLER
Department of Geology, University of New Mexico, Albuquerque, New Mexico 87106, U.S.A.

(*Received* 7 *October* 1971. *Accepted* 14 *November* 1971)

Summary—Niobium, in concentrations as low as 0·02% Nb_2O_5, is determined in a variety of materials without separation or enrichment. Chemical and ionization interferences are controlled, and sensitivity is increased, by maintaining the iron, aluminium, hydrofluoric acid and potassium content within certain broad concentration limits. There is close agreement with the results of analyses by emission spectrographic, electron microprobe and X-ray fluorescence methods.

THE DETERMINATION of niobium by classical wet methods is involved and time-consuming because of the invariable need for separations or extractions. Nearly all the commonly used colorimetric methods require the prior separation of tungsten, molybdenum and titanium.[1] Atomic absorption has not been widely used for the determination of niobium because of the low inherent sensitivity, *e.g.*, Schiller advocated the use of as much as a 60-g sample to analyse steels containing 0·01% niobium.[2] Fortunately, however, there are several chemical species which, over a wide concentration range, enhance the absorption of niobium. This property can be used to advantage to lower the niobium detection limit, because these species provide an "enhancement buffer" over reasonably broad concentration limits. They include aluminium, iron, hydrofluoric acid and the easily ionized alkali metals.

Initially, attempts were made to analyse pandaite ores from Brazil and pyrochlore ores from Canada by the often recommended method of fusion with potassium bisulphate followed by leaching of the melt with hot 4% ammonium oxalate solution or hot 20–30% tartaric acid solution. Most of the Brazilian ores contained pandaite, approximate formula $Ba_{1-x}Nb_2O_{6-x}(H_2O)_{1+x}$, with large amounts of titanium in the form of ilmenite, $FeTiO_3$; also present were aluminium phosphate, the rare earths, quartz, and apatite, along with small amounts of titania.[3,4] Most of the Canadian ores carried very fine-grained uranium-bearing pyrochlore in a silicate-rich matrix such as acmite and potash feldspar. Many other minerals were present, such as calcite, pyrite, pyrrhotite, fluorite, apatite, biotite and magnetite.[5]

The bisulphate fusion of these types of ore proved to be unreliable, presumably owing to the presence of rare earths in the Brazilian ores[1] and uranium in the pyrochlore. Faye reported that uranium in pyrochlore, betafite, euxenite and other niobium-bearing ores led to low niobium results with associated low precision.[6] Faye further found by thorough study of the hydrofluoric acid dissolution method that a mixture of that acid with hydrochloric acid readily dissolved the niobium along with the associated minerals such as ilmenite and magnetite, and that sulphides such as pyrite and molybdenite remained unattacked. The hydrofluoric acid, which interfered with the subsequent ether–thiocyanate spectrophotometric estimation as prescribed by Ward and Marranzino,[7] was removed by evaporation (to a paste) in the presence of phosphoric acid. Faye's hydrofluoric–hydrochloric–phosphoric acid approach was used successfully for the atomic-absorption method in this laboratory, but since hydrofluoric acid greatly enhances the niobium absorption, it was decided to use this to advantage and to eliminate the volatilization of hydrofluoric acid in the presence of phosphoric acid, if possible. This proved to be feasible because the effect of hydrofluoric acid is constant when between 10 and 20% of concentrated hydrofluoric acid are present, the resulting increase in absorption being about 30% (Table I). Teflon beakers eliminate the need for platinum ware, and loss of hydrofluoric acid by its reaction with glassware is circumvented by utilizing polypropylene volumetric flasks. Silica, in the amounts which might remain from incomplete volatilization of silicon tetrafluoride, does not interfere.

Table I.—Effect of alkali metals, aluminium, titanium iron and hydrofluoric acid on 125-μg/ml niobium pentoxide absorption

Added species	Absorption, chart divisions (10 × scale)	
	Without enhancement buffer	With buffer*
—	23	65
K, 500 μg/ml	23·5	64
1000	24	45
2000	24	40
Li, 1000 μg/ml	40	65
Na, 1000 μg/ml	34	65
Rb, 500 μg/ml	40	65
Cs, 500 μg/ml	34	65
Al, 200 μg/ml	53	—
500	60	64
1000	60	—
2000	61	65
3000	63	65
Ti, 500 μg/ml	37·5	63
1500	—	65
500 + Al, 500	—	65
Fe, 500 μg/ml	33	—
1000	36	63
2000	36	—
3000	36	—
HF, 5 ml conc./100 ml	26	—
10	31	65
15	31	—
Fe, 1500 μg/ml	36	—
1500 + HF, 1 ml conc./100 ml	45	—
1500 + 2	47	—
1500 + 10	55	64
1500 + 15	55	—

* 20 ml per 100 ml of solution.

In a thorough investigation of other potential interfering ions in the atomic-absorption determination, it was found that aluminium, iron and the alkali metals also produce enhancement effects, but that these effects can also be controlled (Table I). Aluminium also negates potential interference from titanium, which otherwise would produce low results (if the titanium is not eliminated in the acid attack).

The enhancement from the alkali metals is attributed mainly to the ionization effects of the nitrous oxide–acetylene flame. Manning observed that the best sensitivity for niobium, about 20 μg/ml for 1% absorption, was obtained at 3343·7 Å, and that when 0·1% of potassium was added, a detection limit of 5 μg/ml was achieved.[8] This sensitivity was not attainable on the instrument in this laboratory, but by addition of aluminium, iron, hydrofluoric acid and potassium, a sensitivity of 15 μg/ml could be achieved.

In this laboratory the effect of potassium was not observed to be as great as that reported by Manning, but this is probably because of different burner conditions and because Manning used niobium as the chloride, whereas in this work studies were made with stock solutions of niobium pentoxide which had been dissolved in hydrofluoric and hydrochloric acids.

The effects of other ions were studied, with solutions containing 500 μg of aluminium, 1000 μg of iron and 500 μg of potassium per ml and 5% v/v concentrated hydrofluoric acid. These quantities of additives cause nearly a threefold enhancement of the niobium absorption, and are not critical, since at least twice these amounts can be present without significant change in the enhancement. The absorption of a niobium solution containing between 500 and 3000 μg of aluminium per ml appears to be only 3–5% less than that of a similar solution plus hydrofluoric acid, iron and potassium. The concentrations chosen for these reagents in the enhancement buffer are near the middle of the tolerance ranges, so their presence in samples is without further influence. Table I indicates that large amounts of potassium in the sample begin to reduce the enhancing effect of the combined additives. In the presence of 20 ml of enhancement buffer per 100 ml of sample solution, there was no significant interference with 125 μg of niobium per ml from the following concentrations of other species: TiO_2 or $Na_2HPO_4 \cdot 12H_2O$, 3·0 mg/ml; Mg, 2·5 mg/ml; $Na_2SiO_3 \cdot 9H_2O$, $CaCO_3$, $SrCO_3$, $BaCO_3$, 1·0 mg/ml; Co, Cr, Cu, Mn, Mo, Ni, Ta, U, V, W, or Zn, 200 μg/ml. These were added as solutions of the species named, in hydrochloric, nitric or hydrofluoric acid, or mixtures of these acids.

No interference was observed from a mixture of yttrium plus the rare earths La, Ce, Pr, Nd, Sm and Gd totalling 800 μg/ml. The composition of the mixture was based on the ratio of the abundances of these elements in the earth's crust.[9]

No interference was noted from 5% v/v nitric or sulphuric acid, or from as much as 15% v/v hydrochloric or phosphoric acid, except for the slight reduction in absorbance expected as a result of the change in viscosity.

EXPERIMENTAL

Instrument parameters

The conditions used to achieve optimum sensitivity are listed in Table II. One of the most important factors is the use of wide diameter (0·023 in. bore) tubing to allow a sample uptake rate of 10–12 ml/min. It is felt that many of the conflicting reports of sensitivities, chemical and ionization interferences, *etc*, could be explained if contributors would report aspiration rates, burner heights and flame characteristics. For example, the best niobium sensitivity is obtained with a large uptake rate and the burner head 1–1·5 cm below the light-path. The acetylene and nitrous oxide flow-rates should be set to yield a 1–2 cm high blue flame just above the burner, with an 8–9 cm high "red feather." There is a large reduction in sensitivity for niobium (and tungsten) when the acetylene pressure drops below 50–100 psig. Similar effects, causing erratic results, and attributed to acetone in the acetylene cylinder, have been reported by the Perkin–Elmer Corporation, as for example in the determination of gold with an acetylene–air flame.[10] Niobium sensitivities obtained with other burner and flame types are given by Slavin.[11]

Solutions

Niobium pentoxide, 2000 µg/ml stock solution. Dissolve 1·000 g of pure Nb_2O_5 by warming with 30 ml of 48–50% hydrofluoric acid and 20 ml of concentrated hydrochloric acid in a Teflon beaker.

TABLE II.—INSTRUMENT PARAMETERS

Instrument	Perkin–Elmer, Model 303 with Model 165 recorder
Wavelength	3343·7 Å
Slit	3 (2 Å)
Cathode current	38 mA (40 max)
Scale	10× (for less than 1% Nb_2O_5)
Fuel	Acetylene (9 psig)
Oxidant	Nitrous oxide (40 psig)
Sample uptake rate	10–12 ml/min
Burner height	1–1·5 cm below light-path

After dissolution is complete, dilute to 500 ml with water. Transfer immediately to a polyethylene bottle. This solution is stable for at least 6 months.

Iron solution, 20 *g/l*. Dissolve 20·0 g of pure iron powder in 200 ml of hydrochloric acid (1 + 1) and dilute to 1 litre with water.

Aluminium solution, 10 *g/l*. Dissolve 10·0 g of aluminium powder or fine wire in 200 ml of hydrochloric acid (1 + 1) plus a few drops of 30% hydrogen peroxide and dilute to 1 litre with water.

Potassium solution, 10 *g/l*. Dissolve 19·1 g of reagent-grade potassium chloride in water and dilute to 1 litre.

Enhancement buffer solution. Mix 500 ml each of the iron, aluminium and potassium solutions with 500 ml of 48–50% v/v hydrofluoric acid. Store in a 2-litre polyethylene bottle. This is enough solution for 100 samples and standards.

Standard solutions of Nb_2O_5, 50, 100, 150 and 200 *μg/ml*. Using a polyethylene pipette, transfer 2·5, 5·0, 7·5 and 10 ml of the 2000-μg/ml Nb_2O_5 stock solution into 100-ml polypropylene volumetric flasks. Add 20 ml of enhancement buffer solution and dilute to 100 ml with water. Prepare a blank containing 20 ml of the buffer solution. These solutions are stable for at least 6 months.

Dissolution of sample

Place an accurately weighed 1–2 g sample in a 100-ml Teflon beaker. Rinse the walls with 5–10 ml of water. Add 10 ml of concentrated hydrochloric acid and 10 ml of concentrated hydrofluoric acid and heat the solution for 2 hr on a hot-plate at a temperature low enough to prevent the beaker from sticking to the hot-plate. The solution should not evaporate to dryness, but if it does, repeat the addition of acid and heat to redissolve the niobium. Add 20 ml of the enhancement buffer solution and filter through a Whatman No. 1 paper in a polyethylene funnel into a 100-ml polypropylene volumetric flask. Rinse the beaker and paper with 2–3% v/v hydrochloric acid and dilute to 100 ml with water. Analyse for niobium, using the parameters listed in Table II. Samples containing more than 1% niobium pentoxide can be analysed by preparing more concentrated standards with a corresponding attenuation of the instrument scale.

CONCLUSIONS

The comparison between the atomic-absorption (AA) and two independent X-ray analyses of Canadian niobium-bearing ores is presented in Table III. The two sets of samples, those analysed by AA and laboratory A and those analysed by laboratories A and B are from different drill holes but from the same deposit. The AA results of samples containing less than 0·8% niobium pentoxide agree with the X-ray results from laboratory A within about 4%, but at higher concentrations there is a difference of up to −14%. Results from laboratory B for >0·8% Nb_2 are lower than those from laboratory A by about 6%. This implies that the AA results would agree with those from laboratory B to within 3%.

The results in Table IV show that there is also excellent agreement between the AA and spectrographic analyses for low-grade Brazilian ores. Tables V and VI, respectively, show the comparative results of microprobe analyses and replicate AA analyses of other ores. The results for duplicate analyses of BCS Steel Standard No. 365 were 0·56 and 0·58%. Nb (certificate value 0·57%). The only procedural difference in

TABLE III.—COMPARISON OF AA AND INDEPENDENT X-RAY FLUORESCENCE ANALYSES (LABORATORIES A AND B) OF CANADIAN NIOBIUM-BEARING ORES

Sample	Nb_2O_5, %		Relative difference,* %	Sample	Nb_2O_5, %		Relative difference,† %
	AA	Lab. A			Lab. A	Lab. B	
14	0·24	0·25	−4	25	0·14	0·16	+14
15	0·71	0·77	−8	26	0·26	0·27	+4
16	0·82	0·82	0	27	0·39	0·40	+3
17	0·84	0·88	−5	28	0·45	0·44	−2
18	1·41	1·64	−14	29	0·55	0·56	+2
19	1·76	1·85	−5	30	0·79	0·79	0
20	1·72	1·87	−8	31	0·79	0·77	−3
21	1·91	2·12	−10	32	0·87	0·83	−5
22	2·15	2·44	−12	33	0·95	0·90	−5
23	2·28	2·62	−13	34	0·95	0·92	−3
24	2·50	2·64	−5	35	1·05	1·03	−2
				36	1·63	1·58	−3
				37	1·80	1·73	−4
				38	1·81	1·74	−4
				39	1·95	1·83	−6
				40	1·96	1·83	−8
				41	2·08	1·87	−10

* AA relative to Lab. A.

† Lab. B relative to Lab. A.

TABLE IV.—COMPARISON OF AA AND EMISSION SPECTROGRAPHIC ANALYSES OF BRAZILIAN NIOBIUM-BEARING ORES

Sample	Nb_2O_5, %		Sample	Nb_2O_5, %	
	AA	Spectrographic*		AA	Spectrographic*
1	0·14	0·14	8	0·40	0·29
2	0·12	0·16	9	0·28	0·28
3	0·13	0·13	10	0·42	0·42
4	0·25	0·28	11	0·22	0·22
5	0·31	0·28	12	0·06	0·12
6	0·31	0·32	13	0·23	0·24
7	0·12	0·12			

* Emission spectrographic analyses were performed by Geologia e Sondagens Ltda., Belo Horizonte, Minas Gerais, Brazil.

TABLE V.—COMPARISON OF AA AND ELECTRON MICROPROBE ANALYSES OF BRAZILIAN ORE

Sample	Nb_2O_5, %					
	+100 Mesh		−100 + 200 Mesh		−200 Mesh	
	AA	Probe	AA	Probe	AA	Probe
42	0·47	0·50	0·98	0·81	1·92	2·9*
43	2·40	2·6	2·95	2·3	3·40	2·4*

* Large deviation attributed to insufficient statistical sampling by the electron microprobe analysis.[3]

TABLE VI.—RESULTS OF REPLICATE ANALYSES OF NATURAL AND SYNTHETIC NIOBIUM ORES

Canadian pyrochlore standard (0·5% Nb_2O_5): Nb_2O_5 0·50, 0·45, 0·47, 0·54, 0·50, 0·50, 0·51, 0·50%.

Mean 0·496%, standard deviation = 0·026% (1–2 g samples).

Synthetic rock standards prepared by addition of pure Nb_2O_5 to syenite containing less than 0·02% Nb_2O_5.

1% Nb_2O_5: 0·99, 0·98, 1·02, 1·03% (1–2 g samples)
10% Nb_2O_5: 10·2% (0·2 g sample), 9·7% (0·1 g sample)

TABLE VII.—EFFECT OF NICKEL (ADDED AS $NiCl_2 \cdot 6H_2O$) ON ABSORPTION BY AN 80-μg/ml Nb_2O_5 SOLUTION

Enhancement buffer, *ml*	Ni added, *mg/ml*	Absorption (chart divisions)
0	0	12
20	0	32
20	0·1	31
20	0·5	33
20	2·5	33
20	5·0	23
20	7·5	20

analysing alloys is the addition of 5 ml of concentrated nitric acid per gram of sample to aid in the dissolution. In an attempt to determine the niobium content of an Inconel nickel sample, it was found that concentrations of nickel much greater than 2500 μg/ml begin to reduce drastically the absorption of niobium (Table VII). In such analyses, when the niobium content is low enough to require a dissolved sample with a nickel concentration greater than 0·25 g/100 ml, a prior chemical separation is recommended.

Acknowledgements—The author wishes to thank Paul-Emile Hamelin of the St. Lawrence Columbium and Metals Corporation for the analysed Canadian ore sample, and the University of New Mexico Department of Chemistry for the steel standard. Thanks, also, to Klaus Keil for information on the microprobe and microscopic studies, E. F. Cruft and F. Dubuc for additional information on the ore samples, and R. A. Nash for providing a copy of the spectrographic results.

Zusammenfassung—Niob wird in Konzentrationen bis herunter zu 0,02% Nb_2O_5 in einer Reihe von Materialien ohne Abtrennung oder Anreicherung bestimmt. Man behält chemische und Ionisierungsstörungen im Griff und erhöht die Empfindlichkeit, wenn mann die Gehalte an Eisen, Aluminium, Flußsäure und Kalium innerhalb bestimmter breiter Konzentrationsgrenzen hält. Die Analysenergebnisse stimmen gut überein mit solchen der Emissionsspektrographie, der Elektronen-Mikrosonde und der Röntgenfluoreszenz.

Résumé—On détermine le niobium à des concentrations aussi faibles que 0,02% de Nb_2O_5 dans diverses substances sans séparation ou enrichissement. On contrôle les interférences chimiques et d'ionisation, et la sensibilité est accrue, en maintenant les teneurs en fer, aluminium, acide fluorhydrique et potassium à l'intérieur de certaines larges limites de concentration. Il y a un accord étroit entre les résultats d'analyses par les méthodes de spectrographie d'émission, de microessai électronique et de fluorescence de rayons *X*.

REFERENCES

1. A. R. Powell, *Niobium and Tantalum*, in *Standard Methods of Chemical Analysis* (N. H. Furman, Ed.), 6th Ed., Vol. 1, pp. 714–735. Van Nostrand, Princeton, 1962.
2. R. Schiller, *At. Absorption Newsletter*, 1970, **9**, 111.

3. K. Keil, *Report on Mineralogic, Microscopic, and Electron Microprobe Study of Nb-Bearing Brazilian Soil Samples*, Private investigation, Nov. 28, 1970, 7 pp.
4. E. F. Cruft, personal communication, 1970.
5. F. Dubuc, personal communication, 1971.
6. G. H. Faye, *Chem. in Canada*, 1958, **10**, (4) 90.
7. F. N. Ward and A. P. Marranzino, *Anal. Chem.*, 1955, **27**, 1325.
8. D. C. Manning, *At. Absorption Newsletter*, 1967, **6**, 35.
9. L. H. Ahrens and S. R. Taylor, *Spectrochemical Analysis*, 2nd Ed., p. 218. Addison-Wesley, London, 1961.
10. Perkin–Elmer Corp., *Analytical Methods for Atomic Absorption Spectroscopy*, 1964, Norwalk, Conn.
11. W. Slavin, *Atomic Absorption Spectroscopy*, pp. 137–138. Interscience, New York, 1968.

Talanta, 1972, Vol. 19, pp. 871 to 876. Pergamon Press. Printed in Northern Ireland

CONSTITUTION AND STABILITY OF ACIDIC PERIODATE SOLUTIONS

D. J. B. GALLIFORD*, R. H. NUTTALL and J. M. OTTAWAY®
Chemistry Department, University of Strathclyde, Cathedral Street, Glasgow C.1, Scotland

(*Received* 30 *August* 1971. *Accepted* 14 *November* 1971)

Summary—Acidic periodate solutions are shown to contain two species, tetrahedral IO_4^- and octahedral H_5IO_6. Equilibrium between the two is attained rapidly and the solutions are stable for long periods of time if stored in amber glass bottles.

PERIODATE is a well-established reagent of considerable application in analytical chemistry.[1] It has recently been shown[2] that it is more suitable for the oxidimetric determination of vanadium(IV) than many of the usually preferred oxidants such as permanganate, cerium(IV) or bromate. Many periodate oxidations are also susceptible to trace metal catalysis and these are useful for the determination of very small amounts of catalysts such as ruthenium[3] and chromium.[4] During some recent kinetic and analytical studies of periodate solutions in this laboratory,[2,3] difficulties were encountered from lack of reproducibility in the kinetic results (found to be caused by traces of chromium—as little as 0·01 ppm—adsorbed on the walls of the reaction vessels from chromic acid cleaning mixture) and it became necessary to establish (*a*) the nature of the species present in acidic periodate solutions and (*b*) the stability of the solutions in terms of the total oxidizing power and also in changes in the proportions of the ions with time.

Studies of the nature of periodate solutions have been reported by many authors but rarely do the results obtained relate to the solutions of relatively high ionic strength or high acid concentrations normally used in analytical applications, and many reports are contradictory. Crouthamel *et al.*[5] have shown that spectrophotometric data for solutions of periodic acid and potassium metaperiodate are adequately described by the equilibria

$$H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^- \qquad K_1 = 5{\cdot}1 \times 10^{-4}$$
$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \qquad K_D = 40$$
$$H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^{2-} \qquad K_2 = 2 \times 10^{-7}$$

in the pH range 0–7 and temperature range 0–70°. The important species in acid solutions at pH < 2 are therefore H_5IO_6 and IO_4^-. However, the data are dependent on the assumption that the absorbance at 222·5 nm and pH 5·8 is due to the IO_4^- species only, an assumption which is open to question following the observation that the diffuse reflectance spectrum of solid KIO_4 shows no band at 222·5 nm.[6] The data are also only really satisfactory for solutions of low ionic strength, since anomalous effects, in solutions of higher ionic strength which would significantly alter the values of the equilibrium constants, are ignored. Mishra and Symons[7] have

---

* Present address: May and Baker Ltd., Dagenham, Essex.

also postulated that in strong acid solutions at negative pH, the H_5IO_6 species is further protonated to form $H_6IO_6^+$ or $I(OH)_6^+$ and have reported a pK of $-0{\cdot}8$, in reasonable agreement with a predicted value.

Raman spectroscopy is clearly an advantageous technique for studying the proportions of these species present in solution, since spectra of aqueous solutions can be measured directly, and the observed bands can be assigned on symmetry grounds, and several papers on the Raman spectra of periodate solutions have been reported. Spectra of an 8% aqueous solution of sodium metaperiodate and a 40% solution of paraperiodic acid led Siebert[8] to assign bands at 256, 325, 791 and 853 cm^{-1} to the ν_2, ν_4, ν_1 and ν_3 modes of tetrahedral IO_4^- and bands at 632, 594 and 387 cm^{-1} to ν_1, ν_2 and ν_3 bands of octahedral H_5IO_6. He also concluded that both species were present in equilibrium in both solutions. Chantry and Plane[9] also report that a band at 797 cm^{-1} due to IO_4^- decreases with decrease in pH and, at the same time, a band at 640 cm^{-1} due to H_5IO_6 increases, but no information is given with respect to media or the precise pH used. Infrared spectra of the solid paraperiodic acid and its salts reported by Siebert[10] also lead to the conclusion that these compounds are not hydrates but octahedral species correctly represented by the formulae H_5IO_6, $Na_2H_3IO_6$, *etc.* Keen and Symons[11] have also reported infrared spectra of periodate solutions but suggest that the similarity of spectra to those of $Na_2H_3IO_6$ and $Na_3H_2IO_6$ can only be explained if the major constituent of metaperiodate solutions is not IO_4^- but ions such as $H_4IO_6^-$ or $H_2IO_5^-$.

In this paper we report some investigations of the Raman spectra and stability of periodate solutions, particularly in strongly acid media, in an attempt to provide information for the development of potassium periodate as an analytical reagent.

EXPERIMENTAL

Analytical-reagent grade chemicals were used throughout and water distilled from an all-quartz still was used in the preparation of all solutions.

Preparation of periodate solutions

Using a Stanton automatic recording thermobalance at a heating rate of 6–8°/min, it was found that decomposition of analytical-reagent grade potassium metaperiodate to potassium iodate started in the region of 250°. A temperature of 110° was therefore selected for drying the material and it was found that 0·01% weight loss occurred after one hour at this temperature and that no further loss was recorded after a further four hours' heating. After drying for one hour at 110°, the appropriate weight of KIO_4 was dissolved in distilled water or other media as required. Analytical reagent grade sodium metaperiodate was treated in a similar manner.

Standardization of periodate solutions

Solutions were standardized with reference to sodium arsenite solutions prepared from arsenious oxide.[1,12] An aliquot of the periodate solution was neutralized with sodium bicarbonate and a 3-g excess of bicarbonate were added. Then 3 g of potassium iodide were added and the liberated iodine was titrated with standard 0·025N arsenite.

Raman spectroscopy

Raman spectra were measured on a Cary Model 81 Spectrophotometer equipped with a Spectro-Physics 125 Helium-Neon Laser emitting radiation at 6328 Å. Solid samples were measured in glass vials and solutions in capillary tubes. Solutions for Raman studies were prepared by direct weighing immediately before use, unless otherwise stated.

RESULTS AND DISCUSSION

Stability of periodate solutions

The photodecomposition of periodate to iodate and ozone has been reported[13,14] and has been used for the homogeneous precipitation of thorium iodate.[15] Under more favourable storage conditions, however, periodate solutions are said to be stable for indefinite periods of time.[13,16] To test the effect of various acid media on the long-term stability of periodate solutions, solutions of 0·0125*M* KIO_4 were prepared in distilled water, 0·01*N*, 0·1*N* and 1*N* sulphuric acid, and a 0·4*M* $NaIO_4$ solution was prepared in 5*M* perchloric acid. Half of the solution in distilled water was stored in a screw-cap clear glass bottle and the remaining solutions were stored in screw-cap amber glass bottles, and the bottles were placed on a laboratory shelf in direct natural light. Each solution was standardized at intervals against standard arsenite, as described above, and the results are given in Table I. With the exception of the solution stored in clear glass, no detectable change in potassium periodate concentration was observed over a period of six months. The solution stored in the clear glass bottle deteriorated rapidly over the same period. The sodium periodate solution in 5*M* perchloric acid was stable for only 11–12 days and showed definite signs of decomposition after this, and for kinetic work described elsewhere[2,4] it was necessary to prepare fresh solutions at fortnightly intervals.

TABLE I.—STABILITY OF PERIODATE SOLUTIONS

Titration values (*ml*) for standardization with sodium arsenite. For 0·0125*M* solutions, 50-ml aliquots were titrated with 0·02578*N* sodium arsenite and for the 0·4*M* solution, 6·2-ml portions were titrated with 0·1027*N* arsenite. Storage was in amber glass bottles, except where indicated.

Age, days	0·0125*M* KIO_4 clear glass	0·0125*M* KIO_4	0·0125*M* KIO_4 in 0·01*N* H_2SO_4	0·0125*M* KIO_4 in 0·1*N* H_2SO_4	0·0125*M* KIO_4 in 1*N* H_2SO_4	0·4*M* $NaIO_4$ in 5*M* $HClO_4$
0	48·50	48·50	48·50	48·50	48·50	48·30
3	46·90	48·50	48·50	48·50	48·50	48·30
7	45·00	48·50	48·50	48·50	48·50	48·30
11	—	—	—	—	—	48·30
13	—	—	—	—	—	48·05
15	40·15	48·50	48·50	48·50	48·50	—
18	—	—	—	—	—	46·50
49	19·00	48·50	—	48·50	48·50	—
82	12·50	48·50	—	48·50	48·50	—
190	—	48·50	48·50	48·50	48·50	—

It is therefore established that in a range of neutral and acid media, the total oxidizing power of periodate solutions remains constant for up to six months. It is not clear, however, whether the species present in these solutions remain unchanged during this time.

Raman spectra of periodate solutions

Preliminary studies were carried out with 0·4*M* solutions of sodium periodate in concentrations of perchloric acid from 0·1 to 5*M*. Unfortunately, perchlorate ion exhibits a strong band at 640 cm^{-1} which interfered with an important periodate band and further work was carried out in nitric acid solutions. Careful comparison of the Raman spectra of the periodate species in both acid media indicated that they were essentially identical and that the Raman-active nitrate modes of vibration did not interfere with any periodate bands.

Raman spectra were obtained for solutions of 0·4*M* sodium periodate in distilled water, 0·1, 0·5, 1·0, 3·0 and 5·0*M* nitric acid. Initially, routine spectra were obtained but, following satisfactory interpretation of the observed bands, the solutions were re-examined under the conditions of maximum sensitivity available with the instrument. All solutions were examined immediately after preparation and at intervals over a 3-day period while being stored under air- and light-free conditions and, in addition, stock periodate solutions in perchloric acid were similarly examined. In no case was any change in peak height or peak position observed with time.

The bands observed and their relative intensities are given in Table II and a typical spectrum, *i.e.*, that in distilled water, is shown in Fig. 1A. Four of the five bands observed in neutral aqueous solution correspond closely to those assigned to IO_4^- by Siebert[8] and also correspond to the IO_4^- modes observed in solid KIO_4 and $NaIO_4$, and there seems little doubt as to the validity of this assignment. As the acid concentration is increased, the four bands due to IO_4^- decrease in intensity and the fifth band in distilled water medium at 615 cm^{-1} increases in intensity and shifts to 643 cm^{-1}. In addition, a new band appears at 386 cm^{-1} and also increases in intensity. In 5*M* acid, the bands at 643 and 386 cm^{-1} are the predominant features of the spectrum and only a very weak peak due to IO_4^- remains at 795 cm^{-1}. Operation at the highest available sensitivity shows no additional spectral features in any of the solutions and no new bands are observed on storing the solutions. The spectrum of the commercially available 50% paraperiodic acid solution (Fig. 1B) shows a band at 795 cm^{-1} which must be due to IO_4^- but also shows very strong bands at 386 and 643 cm^{-1} which suggests that the fifth band (615/643 cm^{-1}) in sodium metaperiodate solutions is also due to an octahedral species, in agreement with the observations of Siebert.[8] We were, however, unable to observe the third band required by theory for octahedral symmetry, which Siebert reported at 597 cm^{-1}.

TABLE II.—RELATIVE INTENSITIES OF THE LINES IN THE RAMAN SPECTRUM OF 0·4*M* SODIUM PERIODATE AT VARIOUS NITRIC ACID CONCENTRATIONS

$[HNO_3]$	Relative intensities						
M	860 cm^{-1}	795 cm^{-1}	643 cm^{-1}	615 cm^{-1}	386 cm^{-1}	313 cm^{-1}	270 cm^{-1}
none	19	100	—	2	—	6	9
0·1	6	85	4	—	—	3	5
0·5	3	23	17	—	2	—	—
1·0	—	9	31	—	4	—	—
3·0	—	6	35	—	6	—	—
5·0	—	3	45	—	8	—	—

The Raman spectra, therefore, indicate that two species are present in significant concentrations in acidic periodate solutions. No long-term changes could be observed which might suggest the formation of, for example, peroxides as a precursor of ozone, and use of an oxygen atmosphere had no effect on the spectra. The species are tetrahedral IO_4^- ions in equilibrium with an octahedral species. If the results of Crouthamel *et al.*[5] are even approximately valid for the present media, then at low

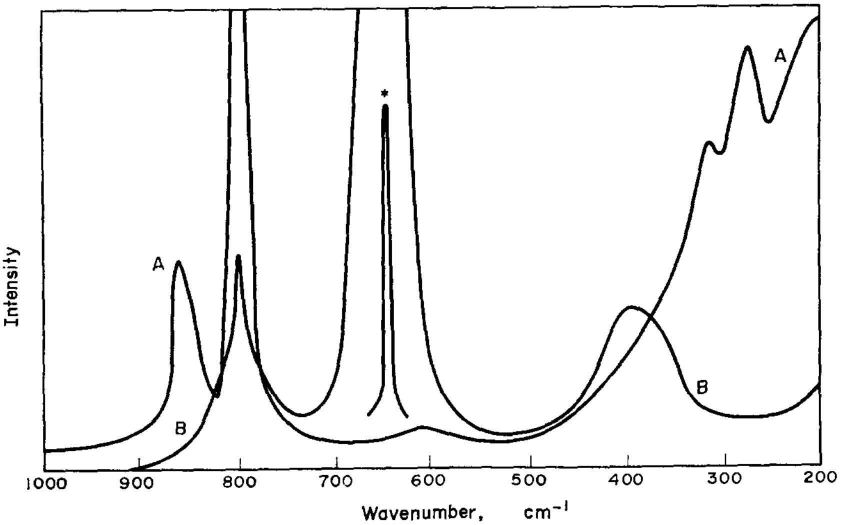


FIG. 1.—Raman spectra of (*A*) 0·4*M* aqueous sodium metaperiodate and (*B*) 50% aqueous paraperiodic acid (H_5IO_6). *(*B*) at reduced sensitivity.

acid concentrations the equilibrium

$$IO_4^- + 2H_2O \rightleftharpoons H_4IO_6^-$$

satisfies the Raman data provided it is assumed that the octahedral species is further hydrated in such a way that either all the oxygen atoms are equivalent or that exchange occurs very rapidly within the vibrational time scale so that the oxygen atoms appear equivalent. As the pH decreases, protonation occurs

$$H_4IO_6^- + H^+ \rightleftharpoons H_5IO_6$$

and the band at 615 cm^{-1} shifts to 643 cm^{-1} and increases in intensity, the equivalence of the oxygen atoms being maintained. As the pH decreases still further, from 1*M* to 5*M* nitric acid, the overall equilibrium,

$$IO_4^- + H^+ + 2H_2O \rightleftharpoons H_5IO_6$$

is pushed even further to the right and the concentration of metaperiodate ions decreases significantly. No evidence was found for the further protonation to $H_6IO_6^+$ but it is possible that this would not be detectable as a separate entity from the other octahedral species, although some further shift of the 643 cm^{-1} band might have been expected.

It is clear that acidic periodate solutions contain a mixture of two species, the proportion of which is dependent on the pH of the solution. From this and other evidence,[18] it is also clear that equilibrium is attained rapidly and that the oxidizing power of such solutions is not altered over at least a six months period. Kinetic evidence[2] suggests that in at least one application the IO_4^- ion is the active oxidizing species and control of pH will be an important factor in this and possibly many other analytical applications of periodate.

Zusammenfassung—Es wird gezeigt, daß saure Perjodatlösungen zwei Spezies enthalten: tetraedrisches JO_4^- und oktaedrisches H_5JO_6. Das Gleichgewicht zwischen beiden stellt sich rasch ein und die Lösungen sind über lange Zeit stabil, wenn sie in braunen Glasflaschen aufbewahrt werden.

Résumé—On montre que les solutions acides de periodate contiennent deux espèces, IO_4^- tetraédrique et H_5IO_6 octaédrique. L'équilibre entre les deux est atteint rapidement et les solutions sont stables pendant de longues périodes de temps si elles sont conservées en flacons de verre teinté.

REFERENCES

1. A. Berka, J. Vulterin and J. Zýka, *Newer Redox Titrants*, Pergamon, London, 1965.
2. D. J. B. Galliford and J. M. Ottaway, *Analyst* in the press. Paper presented at the 3rd International SAC Conference, Durham, 1971.
3. J. M. Ottaway, C. W. Fuller and J. J. Allan, *Analyst*, 1969, **94**, 522.
4. D. J. B. Galliford and J. M. Ottaway, *Analyst* in the press. Paper presented at the 3rd International SAC Conference, Durham, 1971.
5. C. E. Crouthamel, A. M. Hayes and D. S. Martin, *J. Am. Chem. Soc.*, 1951, **73**, 82.
6. T. R. Griffiths, K. A. K. Lott and M. C. R. Symons, *Anal. Chem.*, 1959, **31**, 1338.
7. H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 1962, 1194.
8. V. H. Siebert, *Z. Anorg. Allgem. Chem.*, 1953, **273**, 21.
9. G. W. Chantry and R. A. Plane, *J. Chem. Phys.*, 1961, **34**, 1268.
10. V. H. Siebert, *Z. Anorg. Allgem. Chem.*, 1960, **303**, 162.
11. N. Keen and M. C. R. Symons, *Proc. Chem. Soc.*, 1960, 383.
12. *AnalaR Standards for Laboratory Chemicals*, p. 513. AnalaR Standards Ltd., London, 1967.
13. F. S. H. Head and G. Hughes, *J. Chem. Soc.*, 1952, 2046.
14. H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, 1938, **60**, 2869.
15. M. Das, A. H. A. Heyn and M. Z. Hoffman, *Talanta*, 1967, **14**, 439.
16. G. Dryhurst, *Periodate Oxidation of Diol and Other Functional Groups*, Pergamon, London, 1970.
17. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.
18. K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, 1964, **68**, 3869.

Talanta, 1972, Vol. 19, pp. 877 to 888. Pergamon Press. Printed in Northern Ireland

COMPLEXATION OF POLYVINYL ALCOHOL WITH IODINE

ANALYTICAL PRECISION AND MECHANISM*

J. G. PRITCHARD and D. A. AKINTOLA
North East London Polytechnic, London, E.15, U.K.

(*Received* 16 *July* 1971. *Accepted* 3 *November* 1971)

Summary—Polyvinyl alcohol (PVA), boric acid and tri-iodide form a characteristic blue complex. For a number of PVA samples, prescribed conditions were used to examine the precision of the formation and spectrophotometry of the complex. The precision of calibration curves was 1–2% over the range 0–4 mg of PVA per 50 ml of final solution, over which Beer's law holds. Greater deviations can be caused by faulty preparation and aging of individual PVA solutions. The absorbance is independent of the content of residual acetate groups in the PVA for the range 0–15%. The limit of detection is about 0.01 mg of PVA in 25 ml of sample. A pink colour in the system is due to association of iodine with acetate groups in the PVA. A blue or green colour is due to helical envelopment of iodine molecules by PVA chains stiffened by scattered cyclic groups. The mechanisms of these effects are discussed.

SPECTROPHOTOMETRY of the polyvinyl alcohol(PVA)–borate–iodine complex in aqueous solution is in limited current use for the determination of PVA in paper[1] and biological materials.[2] The blue PVA–iodine complex, first observed in 1927,[3,4] finds use in solid or gel form as the antiseptic "Iodinol" in human and veterinary medicine,[5] and the polarizing[6] and potential superconducting[7] properties of the complex have attracted some attention. In the present work the sensitivity and precision of the spectrophotometric method of analysis are examined over an extended range, and some clarification of the general features of the complex formation is given.

The main conditions chosen for study are those used by Finley,[8] who found that at 690 nm Beer's law was obeyed for the PVA range 0–1 mg/50 ml. This was confirmed with the implication that linearity did not extend beyond the range stated.[9] In our study, the range is extended to 4 mg/50 ml by use of the Hilger and Watts Uvispek spectrophotometer, which accurately covers the wide absorbance range 0–3·2, and the precision of the method is examined in some detail. Also, the effects of residual acetate groups in the PVA are examined quantitatively.

EXPERIMENTAL

Materials

The PVA resins were "Gelvatol" grades 0-60-G, 1-60, 1-90, and 20-90, which have the following weight-average molecular weights and degrees of hydrolysis: 86000, 98·8–100%; 86000, 99–100%; 115000, 99–100%; 125000, 87–89%. Other reagents were of analytical grades.

Calibration-curve solutions

Gelvatol 0-60-G (1 g) was dissolved at 70–80° in *ca.* 100 ml of distilled water, and the solution diluted to 1000 ml in a calibrated flask at room temperature. This stock solution was diluted to give four solutions containing exactly 0·1, 0·15, 0·2, and 0·4 g of PVA per litre. The first two dilutions

---

* Based in part on a report by D. A. Akintola in partial fulfilment of the requirements for the Degree of M.Sc. of the University of London, 1970.

TABLE I.—COMPOSITION OF THE COLORIMETRIC SOLUTION

Component	[Stock solution], *g/l*	*M*	Volume* used, *ml*	Concentration in final solution, *M*
Gelvatol	1·000	0·0227†	4·00§ maximum	0·001816†‡ maximum
Distilled water			~20	
H_3BO_3	40·00	0·6467	15·00	0·1940
I_2	12·70	0·0500	3·00	0·00300
KI	25·00	0·1506		0·00904
Distilled water			to 50·00	

* Per 50·00 ml of final solution.
† Based on CH_2CHOH units.
‡ Successive dilution.
§ Or 4·00 mg/50 ml.

TABLE II.—ABSORBANCES (A_i) FOR VARIOUS PVA CONCENTRATIONS (c_i mg/50 ml) AND DEVIATIONS FOR THE SUCCESSIVE DILUTION OF GELVATOL 0-60-G.

c_i	A_i	$c_i\Sigma A_i/\Sigma c_i$	Deviation*	% Deviation†
0·200	0·135	0·139	−0·004	−2·9
0·400	0·276	0·278	−0·002	−0·7
0·600	0·415	0·416	−0·001	−0·2
0·800	0·562	0·555	+0·007	+1·3
1·000	0·695	0·694	+0·001	+0·1
$A = 0{\cdot}694c$				Mean 1·0‡
0·300	0·204	0·205	−0·001	−0·5
0·600	0·418	0·410	+0·008	+2·0
0·900	0·608	0·615	−0·007	−1·1
1·200	0·805	0·820	−0·015	−1·8
1·500	1·040	1·024	+0·016	+1·6
$A = 0{\cdot}683c$				Mean 1·4‡
0·400	0·308	0·308	0·000	0·0
0·800	0·615	0·616	−0·001	−0·2
1·200	0·915	0·925	−0·010	−1·1
1·600	1·240	1·233	+0·007	+0·6
2·000	1·545	1·541	+0·004	+0·3
$A = 0{\cdot}7705c$				Mean 0·4‡
0·800	0·590	0·615	−0·025	−4·1
1·600	1·300	1·229	+0·071	+5·8
2·400	1·839	1·844	−0·005	−0·3
3·200	2·390	2·458	−0·068	−2·8
4·000	3·100	3·073	+0·027	+0·9
$A = 0{\cdot}768c$				Mean 2·8‡

* $A_i - c_i\Sigma A_i/\Sigma c_i$.
† $100(A_i - c_i\Sigma A_i/\Sigma c_i)\,\Sigma c_i/c_i\Sigma a_i$.
‡ Irrespective of sign.

were from fresh stock solution, the second two from the same stock solution allowed to stand for about four weeks. The composition of the final colorimetric solution is given in Table I. Four sets of solutions were made up to give the ranges of PVA concentration shown in Table II, the PVA being diluted to about 25 ml, then mixed with the boric acid before any iodine was added.

Alternatively, Gelvatol 1-60 and Gelvatol 20-90 solutions containing 0·0100, 0·0150, 0·0200 and 0·0400 g of PVA were made up successively in one particular 100-ml flask, and aliquots were used to make a set of standards as before. Nine standard solutions were prepared from each 100-ml solution in order to determine the scatter due to the complexing reaction and the dilution procedure used in the first approach.

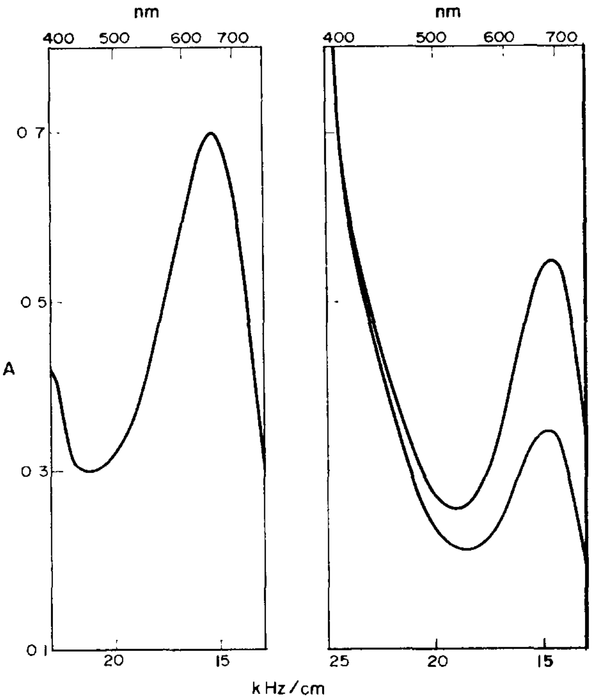


FIG. 1.—Left; spectrum of the complex formed from 1 mg of Gelvatol 1-90/50 ml under the conditions of the analytical method (Tables I and V). The spectrum of Gelvatol 20-90 is the same. Right: spectra given by 1 mg/50 ml, of Gelvatol 1-90 (upper line) and Gelvatol 20-90 (lower line), with 0·194*M* boric acid and 0·0003*M* iodine in aqueous potassium iodide (Table V), *vs.* water.

Spectrophotometry and statistics

Absorbances were measured on the Uvispek at 690 nm *vs.* an appropriate reagent blank, with 1-cm matched cells and suitable slitwidths in the range 0·1–1 mm. The mean of three estimates was taken for each solution, and the instrument was adjusted between each estimate. For each set, the best straight line passing through the origin for absorbance (A) *vs.* concentration of PVA (c) was calculated by the least-squares method. Limits for the true mean values were calculated as $\bar{A}_t \pm ts/3$, where $\bar{A}_i$ is the mean of nine results, s is their standard deviation, and t the value of Gossett's t for 99% confidence.

The spectra of several PVA–iodine combinations with and without boric acid were scanned on a Unicam SP 700 spectrophotometer for Gelvatol 1-90 and Gelvatol 20-90 (*cf.* Figs. 1–3 and Table V). The solutions were made up as for the analytical standards (Table I) except that either 1% or 0·1% Gelvatol and 0·05 or 0·005*M* iodine were used, as appropriate.

RESULTS

The analytical method

Table II gives the results for the successive dilution of the 1 g/l. stock solution of PVA. The best straight lines for the first two ranges give $A = 0{\cdot}69c$. The deviations of the points are random and average about 1%. The results for the other ranges give $A = 0{\cdot}77c$, which is somewhat higher and no doubt reflects the aging of the PVA stock solution. The deviations for these two sets are nearer on average to 2% than 1%, but this average is biased by the first two results in the last range. The deviations are nevertheless quite random. We conclude that Beer's law holds over the complete

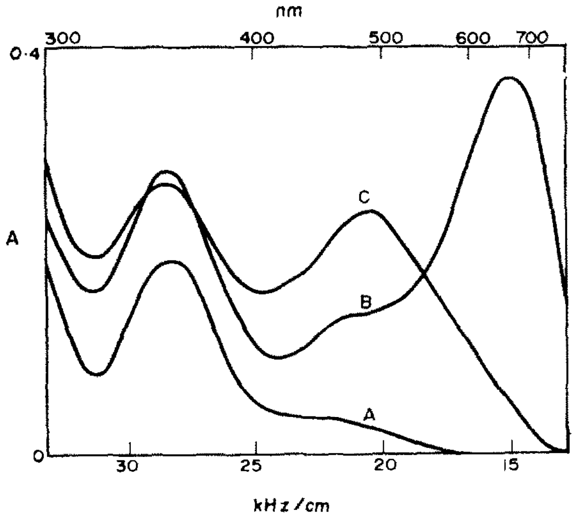


FIG. 2.

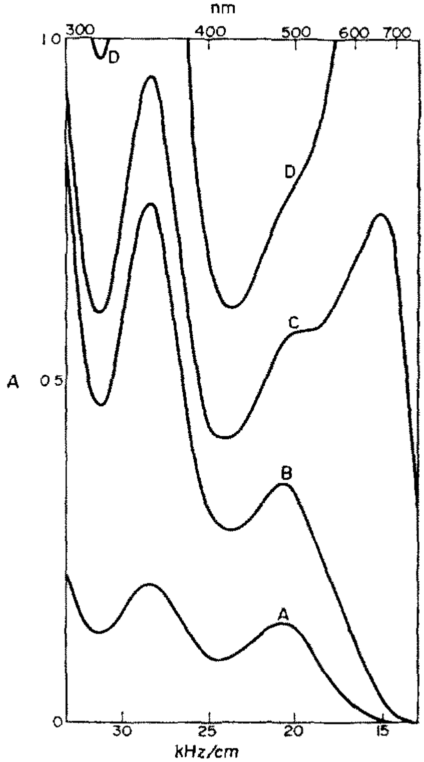


FIG. 3.

FIG. 2.—(A) Spectrum of 0·00005M iodine and 0·00024M potassium iodide. (B) Spectrum formed by 0·0227M Gelvatol 1-90 with 0·194M boric acid, 0·00005M iodine, and 0·00024M potassium iodide (Table V), *vs.* water. (C) Spectrum for Gelvatol 20-90 as in B.

FIG. 3.—(A) Spectrum formed by 0·0227M of Gelvatol 20-90 with 0·00005M iodine and 0·00024M potassium iodide (Table V), *vs.* water. (B) As for A, but with 0·0001M iodine and 0·00048M potassium iodide. (C) As for B, but with the addition of 0·194M boric acid. (D) As for C, but with 0·00015M iodine and 0·00072M potassium iodide.

range. The observed 1–2 % random error arises from a combination of random errors in the dilutions, spectrophotometry and degree of reaction.

Table III summarizes the statistics for Gelvatol 1-60 and Gelvatol 20–90. The deviations are random and average 1 %, which confirms the conclusion that random errors in the dilution, complexing and spectrophotometry do not together greatly exceed 1 %. More critically, Table III shows that the calculated limits of the true mean absorbance for each solution do not exceed ± 1·4 % (99 % confidence) and are random.

The best straight lines passing through the origin, for these results, are given in Table IV. The slopes for the two polymers differ by only about 2 % and agree reasonably with those for the first two sets of results in Table II. The deviations of the individual points are reasonably random. There appears to be no correlation between the deviation and transmittance (I). The possibility of slight curvature in the graphs plotted from Table III is not supported by the good linearity of the results in Table I. However, the deviations of the individual points average 4–5 % owing to combination

TABLE III.—LIMITS OF THE TRUE MEAN AND DEVIATIONS FOR SETS OF NINE MEASUREMENTS OF ABSORBANCE (A_i) FOR INDEPENDENT DILUTIONS

c_i *mg**	Mean A_i $\bar{A}_i$	Limits of true mean†	% Limits‡	Mean deviation§	Mean % deviation
Gelvatol 1-60					
1·00	0·741	±0·013	±1·8	0·009	1·2
1·50	1·072	0·012	1·1	0·009	0·8
2·00	1·472	0·015	1·0	0·012	0·8
3·00	2·100	0·017	0·8	0·012	0·6
4·00	2·659	0·053	2·0	0·040	1·5
			Mean 1·3		Mean 1·0
Gelvatol 20-90					
1·00	0·615	0·008	1·2	0·005	0·9
1·50	1·030	0·016	1·2	0·011	1·1
2·00	1·440	0·017	1·2	0·011	0·8
3·00	2·250	0·031	1·4	0·021	0·9
4·00	2·890	0·053	1·8	0·038	1·3
			Mean 1·4		Mean 1·0

* Mg/50 ml

† 99% Confidence limits.

‡ $100ts/3\bar{A}_i$.

§ Mean of the set of nine values of $|A_i - \bar{A}_i|$.

of random general error (1–2%, as above), weighing error of the small samples, and any inhomogeneity of the PVA.

General spectrophotometry

Figure 1 shows a scan of the well-defined spectral peak of the PVA–borate–iodine complex measured *vs.* the reagent blank. At the concentrations of iodine and iodide used, the reference solution absorbs so strongly ($A_{520} \sim 1{\cdot}0$; $A_{645} \sim 0{\cdot}1$), that a scan *vs.* water instead of the reagent blank does not distinguish the absorption band due to

TABLE IV.—DEVIATIONS FROM STRAIGHT LINES IN THE INDEPENDENT DILUTION EXPERIMENT

c_i	$\bar{A}_i$	I (%)	$c_i\Sigma\bar{A}_i/\Sigma c_i$	Deviation*	%Deviation†
Gelvatol 1-60					
1·00	0·741	18·15	0·699	+0·042	+6·0
1·50	1·072	8·48	1·049	+0·023	+2·2
2·00	1·472	3·37	1·399	+0·073	+5·2
3·00	2·100	0·79	2·098	+0·002	+0·1
4·00	2·659	0·22	2·797	−0·138	− 4·9
$A = 0{\cdot}699c$					Mean 3·7‡
Gelvatol 20-90					
1·00	0·615	24·26	0·715	− 0·100	− 14·0
1·50	1·030	9·33	1·073	− 0·043	− 4·0
2·00	1·440	3·63	1·431	+0·009	+0·6
3·00	2·250	0·56	2·146	+0·104	+4·8
4·00	2·890	0·13	2·862	0·028	+1·0
A $0{\cdot}715c$					Mean 4·9‡

* Deviation $= \bar{A}_i - c_i\Sigma\bar{A}_i/\Sigma c_i$.

† Percent deviation $= 100(\bar{A}_i - c_i\Sigma\bar{A}_i/\Sigma c_i)\Sigma c_i/c_i\Sigma\bar{A}_i$.

‡ Irrespective of sign.

the complex. Only a small fraction of the iodine reacts to form the complex. The yellow-green colour of the colorimetric solution is due to absorption of almost all of the blue incident light by unreacted iodine and of the red by complex, which leaves a window around 480 nm. The scans for Gelvatol 1-90 and Gelvatol 20-90 under the conditions chosen for the analysis are almost identical and reveal no dependence on the different acetate-group contents. However, this is not true for other conditions.

Table V contrasts the colour effects observable with Gelvatols 1-90 and 20-90 for various concentrations of the PVA and iodine, both in the presence and absence of boric acid. When the iodine concentration is reduced by a factor of 10 the amount of complex formed by the two polymers is markedly different (Fig. 1), that for Gelvatol 20-90 being reduced the more. Some most interesting effects are revealed when the iodine concentration is reduced further by a factor of six and the PVA concentration is increased to a large excess over the iodine. The polymer with 12% residual acetate groups shows an absorption band with $\lambda_{max} = 482$ nm associated with a reddish colour, whether boric acid is present or not, provided that the iodine concentration is low enough (Figs. 2 and 3). However, at higher iodine concentrations and in the presence of boric acid, the absorption band with $\lambda_{max} \sim 680$ nm associated with the blue complex also appears prominently and becomes very intense for iodine concentrations much in excess of $10^{-4}M$. In contrast (Fig. 2), the polymer with only 0–1% residual acetate groups shows in the presence of boric acid a prominent blue colour even for the lowest final iodine concentrations, provided that the iodine solution has a concentration not less than about 0·005*M when it is added.* When 0·0005*M* iodine solution is used, no colour reaction is observed: also, the amount of colour developed

TABLE V.—COLOUR REACTIONS OF GELVATOLS 1–90 AND 20-90 WITH IODINE, WITH AND WITHOUT 0·194*M* BORIC ACID

Final [PVA] *M**	Final [iodine] *M*	Colour reaction Gelvatol 1-90 (~½% CH_3·CO gps.)	 Gelvatol 20-90 (~12% CH_3·CO gps.)	Spectrum
With 0·194*M* boric acid				
—	0·003†	(Orange)		
0·00045	0·003†	Dark yellow-green	Dark yellow-green	Fig. 1
—	0·0003	(Yellow)		
0·00045	0·0003	Bottle green	Grass green	Fig. 1
0·00136	0·0003	Dark turquoise-blue	Dark turquoise-blue	
—	0·00005	(Very pale yellow)		Fig. 2
0·0227	0·00005	Copper-sulfate blue	Violet-pink	Fig. 2
0·0227	0·0001	Dark blue‡	Violet-blue	Fig. 3
0·0227	0·00015	Dark blue‡	Deep violet-blue	Fig. 3
Without boric acid				
0·0227	0·00005	Pale yellow§	Rosé wine	Fig. 3
0·0227	0·0001	Pale yellow§	Rosé wine	Fig. 3
0·0227	0·001	Yellow-orange§	Brown	
0·0227	0·01†	Gradual, deep green	Yellow-brown§	
0·227	0·01†	Dark green → blue	Dark yellow-brown ¶	

* With respect to CH_2CHOH units.

† Stock solution contained 0·05*M* I_2 and 0·15*M* KI, as for the colorimetric solution; otherwise it was 0·005*M* I_2 and 0·024*M* KI.

‡ Off scale on Fig. 3.

§ No effect.

¶ Green shade after two days.

when the $0{\cdot}005M$ iodine solution is used appears to depend on its rate of dilution when added to the PVA–borate solution. There is, therefore, a kinetic effect which appears to dictate the final colour of the homogeneous solution. A small amount of absorption at 500 nm is also shown by the almost fully hydrolysed polymer (Fig. 2).

When there is no boric acid, the polymer with 12% of acetate groups shows only the broad 482-nm absorption band for low iodine concentration, whereas the almost fully hydrolysed polymer does not react at low iodine concentration. Only when treated with $0{\cdot}01M$ iodine would the latter polymer *slowly* develop a deep green colour, again clearly indicating a kinetic effect in which the "blue" complex is slowly formed. The green colour is, of course, due to a combination of the absorption of violet and blue light by unreacted iodine and the absorption of red and yellow light by the "blue" complex; when the PVA concentration is high, most of the iodine reacts to form complex and the colour of the solution is deep blue. The 12% of acetate groups inhibits formation of the blue complex when boric acid is absent.

DISCUSSION

The colorimetric method

We can accept the equation $A = 0{\cdot}70c$ as representing the absorbance of fresh PVA solutions at 690 nm to within about 2% (c in mg/50 ml). The equation is independent of the amount of residual non-hydrolysed acetate groups in the PVA, up to at least about 15%. This is important because the majority of commercial PVA's are not completely hydrolysed, but only substantially so. The equation applies to molecular weights near 10^5. If the minimum detectable absorbance is taken as 0·007, this establishes the limit of detection as 0·01 mg of PVA in 25 ml of sample solution (50 ml of colorimetric solution).

Some limitations of the method are evident. To achieve the 1–2% operator–instrument precision, solutions of unknowns and standards should be fresh and uniformly prepared from samples weighing at least 0·1 g. Several solutions of an unknown sample should be prepared and analysed to check that reproducibility is indeed within 2%. We have noted that a small amount of insoluble, fibrous dark-blue complex can sometimes precipitate during the analysis, especially in the case of polymers with high molecular weights. This causes a low result, and such analyses should be discarded. The accuracy is likely to be limited from this cause in the case of unknown samples of PVA which contain a substantial fraction of high-molecular-weight "tail", which can be relatively easily precipitated in aqueous solution by boric acid.

The degree of intramolecular cyclic borate formation for PVA in aqueous solution can generally approach 20% before intermolecular borate formation gels the polymer.[10] Under the conditions of the present method, approximately this semi-saturation level of intramolecular borate formation should be achieved, and it is plausible that 10–15% of acetate groups should not interfere. If the iodine level is high enough, ~ 12% of acetate groups does not interfere, but if the iodine level is low or borate is absent, notable effects of acetate groups are observed (Table V). As the PVA : borate ratio is increased, the degree of cyclic borate formation possibly decreases, the more so with increase in acetate-group content, but the main effect at low iodine concentration is the preferential formation of the red type of complex which robs the system of iodine that would otherwise be available for formation of the blue complex. These effects are not important under the conditions of the analytical method which, within limits, is independent of the preparative history of the PVA sample. However, it appears likely that eventually, at perhaps 30–40% of acetate groups, the freedom of the analytical method from dependence on the acetate content of the polymer must break down. We might also note that in the case of relatively small amounts of borate, order-of-mixing effects apparently preclude an accurate method for the determination of borate via the PVA–borate–iodine complex.[11]

General characteristics of PVA–iodine complex formation

In the absence of boric acid, complex formation at room temperature, for sufficiently high concentrations of aqueous iodine, potassium iodide, and well-hydrolysed PVA, involves the slow development of a blue or green colour characterized by $\lambda_{max} \sim 620$ nm. Under some conditions, the maximum absorbance and a state of apparent equilibrium are not achieved for some days, and the kinetics and a number of other characteristics of this reaction continue to attract interest.[12–15] The degree of blue colour at equilibrium has been shown to depend very much on structural features of the PVA such as (it would appear at first sight) its tacticity.[12,16,17] The addition of sufficient boric acid to the PVA–I_2–KI system removes the dependence of the absorbance on time and tacticity.[12] In the absence of boric acid, PVA deliberately substituted with cyclic acetal or formal groups produces the usual blue complex, which is strikingly more intensely coloured as the degree of acetal or formal substitution increases.[18]

Our main results show that random substitution of one acetate group for one hydroxyl group in eight along the PVA chain has essentially no effect on the formation of the blue PVA–borate–iodine complex provided that a large excess of both iodine and boric acid is present. However, this fraction of acetate groups is sufficient to attenuate seriously the formation of the blue complex for iodine: PVA ratios of about 1 or more even in the presence of boric acid (Fig. 2). Furthermore, we have shown that the presence of acetate groups leads to *preferential* formation of a "red" complex characterised by $\lambda_{max} \sim 500$ nm, whether boric acid is present or not (Fig. 3). The formation of such red colours has been observed previously,[19,20] and even in the case of some specimens of so-called "fully" hydrolysed PVA, when its concentration is relatively high, *e.g.*, for 1% PVA (0·23*M*) with 0·001*M* iodine and 0·002*M* iodide, a red colour is reported to be produced with $\lambda_{max} \sim 500$ nm.[15] These red complexes formed in aqueous solution are almost certainly closely related to the red-violet complex formed when a methanolic solution of polyvinyl acetate and iodine is added to an aqueous solution of potassium iodide.[21,22]

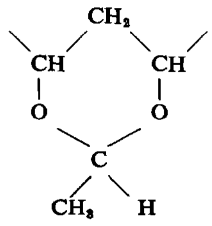
The red acetate complex

Clearly the red complex is associated with the acetic ester function in PVA. As it is extremely difficult to remove the last traces of acetate groups from PVA, this polymer may show the red reaction in solution whenever the acetate: iodine ratio is sufficiently high and other conditions are suitable. Before the borate reaction was known, the formation of this red colour was proposed as the basis of an analytical method for PVA.[23] It cannot be reliable, because the intensity of colour depends on both the concentration of the PVA and the fraction of acetate groups it contains.

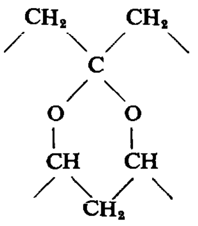
In seeking a model for the red complex, we must remember that the orange-brown colour of aqueous solutions of iodine is due to a complex of the "ether" type in which an iodine molecule is loosely bonded to the unshared electrons of bivalent oxygen.[24,25] Thus, a solution of pure iodine in water shows a broad absorption band with λ_{max} = 459 nm in the visible region, associated with $H_2O{\cdot}I_2$, and two less intense bands in the ultraviolet region with λ_{max} = 288 and 352 nm associated with the formation of I_3^- and IO^- ions (see below). In the presence of an excess of potassium iodide, the intensities of the latter two bands are very strongly enhanced, leaving the 459-nm $H_2O{\cdot}I_2$ band merely as a "tail" at the side of the 352-nm band, so that the solution appears yellow when dilute (Fig. 2) and orange-red when concentrated. Unperturbed iodine in carbon tetrachloride solution has a single band with λ_{max} = 516 nm, which gives a pink-violet colour. Models of the rather convoluted polyvinyl acetate and partially acetylated PVA molecules show that they possess cells in which an iodine molecule can fit in association with one set of ether-oxygen orbitals. Bonding of the "acetone" type[24] to the π-bonding orbitals of the carboxyl oxygen also appears possible. We conclude that the type of absorption in the 460-nm region due to $H_2O{\cdot}I_2$ is enhanced and its wavelength slightly increased when iodine is chemisorbed at the ester-oxygen functions in PVA polymers (Fig. 3).

The blue complex

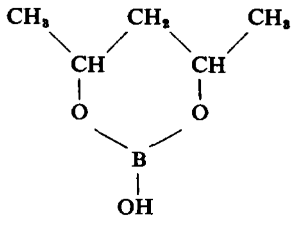
This complex is circumstantially connected with the formation of cyclic acetal and cyclic borate groups in PVA. Small proportions of acetal groups are always present in PVA prepared from vinyl acetate, because partial hydrolysis of this monomer is difficult to avoid and yields acetaldehyde which acetalates the PVA ultimately prepared. It is also difficult to prepare PVA in the entire absence of oxygen, which introduces keto groups along the chain and aldehyde end groups, and these can yield cyclic ketal and acetal links between PVA chains by a slow acid-catalysed reaction.[6] Thus, the observed source-dependence of the absorbance intensity of the PVA–iodine complex in the absence of boric acid most probably arises from different numbers and types of cyclic acetal (**1**) and ketal (**2**) structures. The kinetics of complex formation may also be affected by these structures, as discussed later.



(1)



(2)



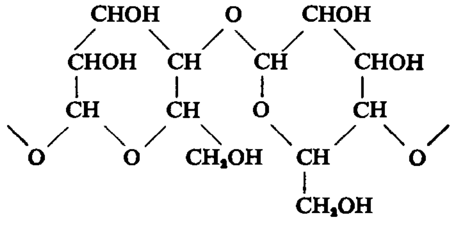
(3)

Mechanism of formation of the blue complexes

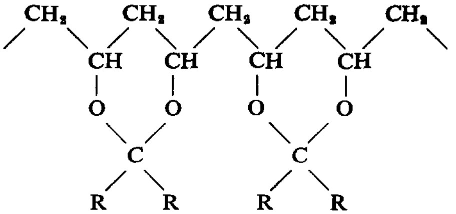
The PVA–iodine complex probably has a similar structure to the better understood amylose–iodine complex, *i.e.*, long straight chains of associated iodine molecules are crystallized down the centres of helical amylose chains.[7,26] We have shown that 2,4-dihydroxypentane cyclic borate ester[27] (3) does not react with our iodine–iodide stock solution. The formation of the PVA–borate–iodine complex therefore requires the concerted effect of many segments of the borated PVA chain. It can be argued that the amylose molecule can crystallize easily in helical form, enveloping a string of iodine molecules, because the backbone of this polymer (4) lacks complete flexibility. We take the view that any microcrystallization of pure PVA in aqueous solution should occur in the stacked planar zig-zag form, as observed for aqueous gels of PVA.[28] Helical crystallization should only be possible if the flexibility of the PVA chain is reduced, through formation of cyclic groups, to give a structure somewhat analogous (5) to that of amylose. This would, of course, prevent zig-zag crystallization for these substituted segments and several adjacent ones. Thus, partial acetalation or boration of the PVA chain may remove degrees of freedom of movement sufficiently to permit formation of the first turn of the helix in conjunction with iodine.

Recent kinetic studies of the very rapid formation of the blue amylose–iodine complex ($\lambda_{\max} \sim 630$ nm) show reaction orders of one with respect to amylose and four with respect to iodine and tri-iodide ions considered together.[29] This suggests that I_8 may be complexed, no doubt in stages. The observation of threshold concentrations of iodine required for complex formation with PVA is consistent with a high-order dependence of this reaction on iodine concentration. No reaction can be detected with $10^{-4}M$ iodine in the presence of boric acid, and in its absence about $10^{-2}M$ iodine is needed for a slow reaction to ensue at such cyclic sites as there are. The latter reaction is inhibited by 12 % of acetate groups in the case of Gelvatol 20-90.

The tri-iodide ion appears necessary for the successful production of the blue complex, although the latter can be formed without deliberately added iodide ions,

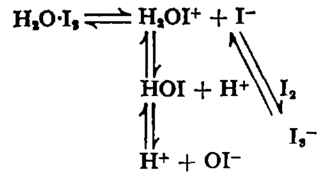


(4)



(5)

especially in the presence of plenty of boric acid.[30] Iodine in aqueous solution generates a small quantity of its own I_3^- ions:



The I_3^- ion is linear, stable, and abundant in aqueous iodine–iodide solutions and may well provide the matrix on which the first turns of the PVA helix can wind. A likely mechanism for the formation of the helical complex would be:

$$\begin{aligned} &\text{Helix-}I_3^- + I_2 \rightarrow \text{Helix-}I_4 + I^- \\ &\text{Helix-}I_4 \;+ I_3^- \rightarrow \text{Helix-}I_7^- \\ &\text{Helix-}I_7^- + I_2 \rightarrow \text{Helix-}I_8 + I^-. \end{aligned}$$

It appears unlikely that ions such as I_5^-, I_7^-, or I_9^- occur in the final complex. Such ions do exist, for example, in the tetramethylammonium salts (which are no doubt ion-paired in solution), but they absorb strongly over the complete visible range, and more so in the range 400–600 nm, so that they are very deep red in colour when viewed by transmitted light.[31,32]

The shift from $\lambda_{max} = 516$ nm in the unperturbed iodine molecule to 459 nm in the iodine–water complex represents an increase of 7 kcal/mole in the energy of the electronic transition. This is associated with a slight extension of the I–I bond when co-ordinated to oxygen.[24] The formation of the blue complexes between iodine and amylose, starch, and PVA represents a change from iodine–solvent complexation to $(I_2)_n$ chemisorption in which the iodine is protected from complexing oxygen groups by a helix of hydrocarbon groups. This change is associated with a decrease of 9–14 kcal/mole in the energy of the transition compared to unperturbed iodine, and this may be related to a corresponding compression of the I–I bonds within the helix.

Zusammenfassung—Polyvinylalkohol (PVA), Borsäure und Trijodid bilden einen charakteristischen blauen Komplex. Bei einer Anzahl von PVA-Proben wurden konstante Bedingungen angewandt, um die Reproduzierbarkeit der Bildung und des spektrophotometrischen Verhaltens des Komplexes zu prüfen. Die Reproduzierbarkeit der Eichkurven betrug 1–2% im Bereich 0–4 mg PVA pro 50 ml endgültig zubereiteter Lösung; in diesem Bereich gilt auch das Beersche Gesetz. Größere Abweichungen können durch fehlerhafte Präparation und Alterung einzelner PVA-Lösungen vorkommen. Im Bereich 0–15% ist die Extinktion unabhängig vom Gehalt des PVA an restlichen Acetatgruppen. Die Nachweisgrenze liegt bei etwa 0,01 mg PVA in 25 ml Probe. Eine Rosafärbung des Systems beruht auf Anlagerung des Jods an Acetatgruppen im PVA. Blau- oder Grünfärbung kommt durch schraubenförmige Einschließung von Jodmolekülen durch PVA-Ketten zustande, die durch cyclische Gruppen hier und da versteift werden. Die Mechanismen dieser Effekte werden diskutiert.

Résumé—L'alcool polyvinylique (PVA), l'acide borique et le triiodure forment un complexe bleu caractéristique. Pour un certain nombre d'échantillons de PVA, on a utilisé les conditions prescrites pour examiner la précision de formation et de spectrophotométrie du complexe. La précision des courbes d'étalonnage est de 1–2% dans le domaine 0–4 mg de PVA pour 50 ml de solution finale, domaine dans lepuel la loi de Beer est suivie. Des écarts plus grands peuvent être causés par une préparation et un vieillissement défectueux de solutions particulières de PVA. L'absorption est indépendante de la teneur en groupes acétate résiduels du PVA pour le domaine 0–15%. La limite de détection est d'environ 0,01 mg de PVA dans 25 ml d'échantillon. Une coloration rose du système est dûe à l'association de l'iode avec les groupes acétate dans le PVA. Une coloration bleue ou verte est dûe à l'enveloppement hélicoïdal de molécules d'iode par des chaînes de PVA rigidifiées par des groupements cycliques dispersés. On discute des mécanismes de ces influences.

REFERENCES

1. M. Samkova and G. Milchova, *Papir Celul.*, 1967, **22**, 337; *Chem Abstr.*, **68**, 106161.
2. S. Ishikawa and Y. Yamatani, *Nippon Nogei Kagaku Kaishi*, 1968, **42**, 165; *Chem. Abstr.*, **69**, 25769.
3. W. O. Herrmann and W. Haehnel, *Berichte*, 1927, **60**, 1658.
4. H. Staudinger, K. Frey and W. Starck, *ibid.*, 1927, **60**, 1782.
5. V. O. Mokhnach, *Iodinol Med. Vet.*, *Eksp. Klin. Issled.*, *Akad. Nauk SSSR*, *Bot. Inst.*, 1967, 5; *Chem. Abstr.*, **68**, 43119.
6. J. G. Pritchard, *Poly(vinyl alcohol)-Basic Properties and Uses*, Gordon and Breach, New York, 1970.
7. W. A. Little, *J. Polymer Sci.*, *C*, 1970, No. 29, 25.
8. J. H. Finley, *Anal. Chem.*, 1961, **33**, 1925.
9. M. Chene, O. Martin-Boret and M. Clevy, *Papeterie*, 1966, **88**, 273.
10. S. Saito, H. Okuyama, H. Kishimoto and Y. Fujiyama, *Kolloid-Z.*, 1955, **144**, 41.
11. C. A. Pannuti, V. D. Lynch, A. J. Monte-Bovi and J. J. Sciarra, *J. Pharm. Sci.*, 1966, **55**, 535.
12. M. M. Zwick, *J. Appl. Polymer Sci.*, 1965, **9**, 2393.
13. L. G. Tebelov, *Tr. Molodykh Uchenykh, Saratovsk. Univ.*, *Vyp. Khim.*, *Saratov*, 1965, 156; *Chem. Abstr.*, **65**, 7300.
14. L. G. Tebelev and A. N. Silkina, *Protsessy Geleobrazovaniya*, 1968, 32; *Chem. Abstr.*, **71**, 81979.
15. K. Bolewski and A. Buraczewska, *Acta Pol. Pharm.*, 1970, **27**, 33; *Chem. Abstr.*, **73**, 88281.
16. K. Imai and M. Matsumoto, *J. Polymer Sci.*, 1961, **55**, 335.
17. K. Yamaura, S. Matsuzawa and Y. Go, *Kobunshi Kagaku*, 1969, **26**, 265; *Chem. Abstr.*, **71**, 22411.
18. S. Hayashi, M. Takayama and C. Kawamura, *Kogyo Kagaku Zasshi*, 1970, **73**, 412; *Chem. Abstr.*, **73**, 4287.
19. S. A. Miller and A. Brakken, *J. Chem. Soc.*, 1951, 1933.
20. S. Hayashi and K. Takizawa, *Kogyo Kagaku Zasshi*, 1968, **71**, 2051; *Chem. Abstr.*, **70**, 48172.
21. S. Hayashi and C. Kawamura, *ibid.*, 1969, **72**, 2491; *Chem. Abstr.*, **72**, 122206.
22. S. Hayashi, C. Kawamura and M. Takayama, *Bull. Chem. Soc. Japan*, 1970, **43**, 537.
23. F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Vol. III, 3rd Ed., p. 54. Van Nostrand, New York, 1953.
24. R. S. Mulliken, *J. Am. Chem. Soc.*, 1950, **72**, 600.
25. R. C. Brasted, *Comprehensive Inorganic Chemistry* (Sneed, Maynard, and Brasted, Series Eds.), Vol 3, Chap. 4. Van Nostrand, Princeton, 1954.
26. M. M. Zwick, *J. Polymer Sci.*, *A*-1, 1966, **4**, 1642.
27. J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.
28. G. Rehage, *Kunststoffe*, 1963, **53**, 605.
29. J. C. Thompson and E. Hamori, *Biopolymers*, 1969, **8**, 689.
30. V. O. Mokhnach and I. P. Zueva, *Dokl. Akad. Nauk SSSR*, 1964, **155**, 846; *Chem. Abstr.*, **61**, 1961.
31. S. Kusabayashi, H. Mikawa, S. Kawai, M. Uchida and R. Kiriyama, *Bull. Chem. Soc. Japan*, 1964, **37**, 811.
32. F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, 1923, **123**, 654.

Talanta, 1972, Vol. 19, pp. 889 to 894. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Liquid–liquid interfaces as potentiometric ion-sensors—I
The n-butanol–water interface as indicating sensor for the potentiometric titration of some acids and bases

(*Received* 20 *May* 1971. *Accepted* 5 *January* 1972)

The interface between two immiscible liquids must function as an indicating electrode because the concentration of a particular ion will be different on the two sides of the interface. The literature mentions only an attempt at potentiometric titration of some acids and bases[1] by use of benzene, toluene, chloroform and nitrobenzene interfaces with water.

Here we present the results of titrations of some acids and bases, with the n-butanol–water interface as indicating electrode. The titrations were performed in a cell with a base area of ~ 20 cm^2, the solution to be titrated being covered with a layer of water-saturated n-butanol about 5 mm thick.

The potential on both sides of the interface was monitored by two calomel electrodes, to give the e.m.f. of the following cell (Fig. 1):

(+) S.C.E.—n-butanol | aqueous solution—S.C.E. (−)

The electrode functions obtained by titrating 0·1*N* hydrochloric, nitric, perchloric and sulphuric acids with 1*M* potassium hydroxide are given in Fig. 2. The corresponding pH values were simultaneously measured with a glass electrode. For the first three acids similar electrode functions were obtained. For sulphuric acid a different shape was observed, perhaps because of the influence of the anion.

Figure 3 gives the titration curves of these four acids and 0·1*N* phosphoric acid. They do not have the shape of classical potentiometric titration curves—their slope for sulphuric acid differs from the

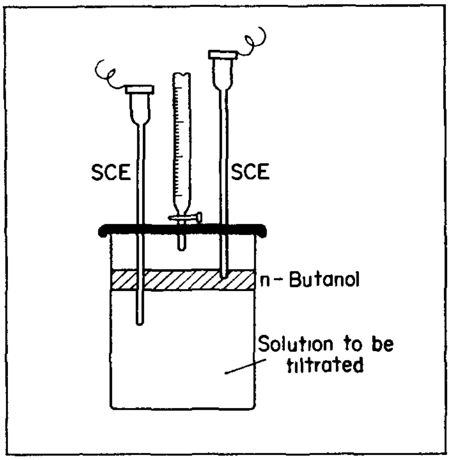


Fig. 1.—Titration cell.

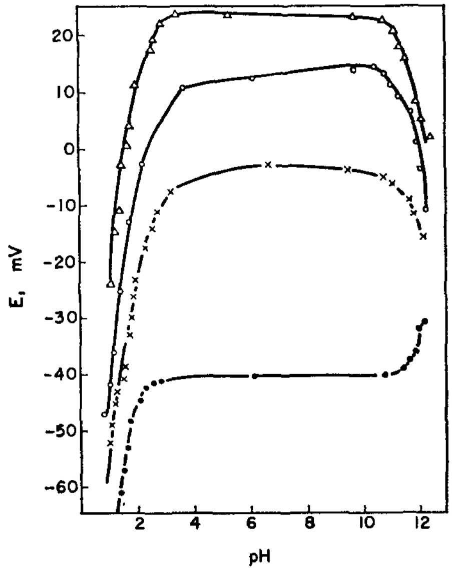


Fig. 2.—Electrode function.
—×— HCl —Δ— HClO$_4$
—○— HNO$_3$ —●— H$_2$SO$_4$

others in shape and in potential change. Table I gives comparative results for titration of acids by this potentiometric method and with a pH-meter.

Figure 4 shows titration curves for hydrochloric acid of different concentrations. The equivalence point can easily be located for concentrations down to $10^{-3}M$. Increasing the electrolyte concentration decreases the slopes of the two branches of the titration curve, but the equivalence point can still be located even for $5M$ potassium chloride media (Fig. 5).

TABLE I.—Titration of $0{\cdot}1N$ acids with $0{\cdot}1M$ KOH

Acid	Titration, *ml*	
	Glass-electrode*	n-Butanol–water interface
HCl	3·95	3·93
H_2SO_4	5·90	5·75
HNO_3	4·06	4·06
$HClO_4$	4·22	4·15
H_3PO_4	5·32	5·25†

* Hahn-Weiler location of end-point.

† Only the first step of neutralization was observed.

The influence of surface-active substances on the titration of $0{\cdot}05M$ hydrochloric acid with $0{\cdot}5M$ potassium hydroxide was also investigated (Fig. 6). In the presence of surfactant anions the position

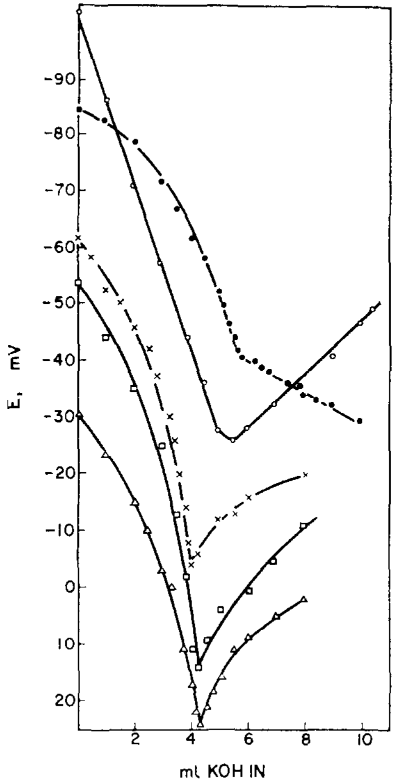


FIG. 3.—Titration curves of acids.
—×— HCl —●— H_2SO_4
—□— HNO_3 —○— H_3PO_4
—△— $HClO_4$

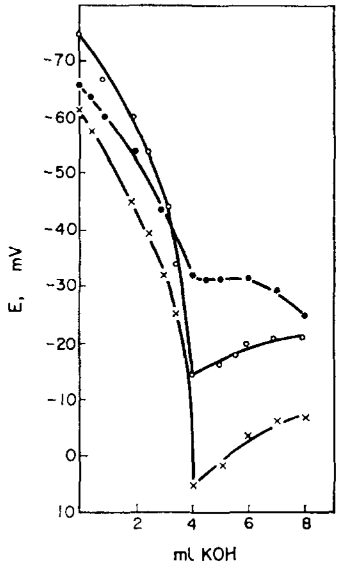


FIG. 4.—Titration curves of HCl of different concentrations.
—×— lo^{-1}*M*; —○— lo^{-2}*M*; —●— lo^{-3}*M*.

of the equivalence point remains practically the same but the shape of the curve changes, there being a pronounced minimum. In the presence of surfactant cations (*e.g.*, alkyl pyridinium ions) both the shape of the curve and the position of the equivalence point are affected, most probably because of consumption of hydroxide by the surface-active substance. Neutral surface-active substances (*e.g.*, polyvinyl alcohol) have no influence.

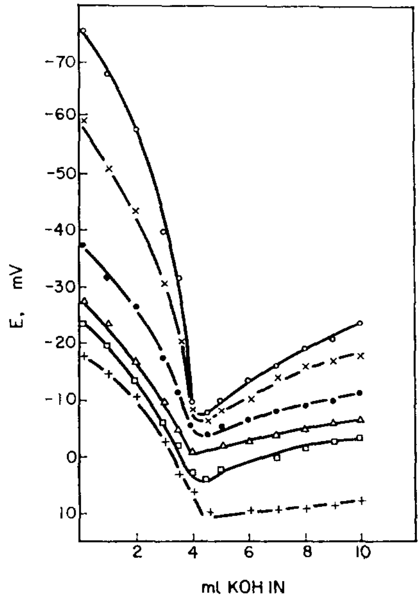


FIG. 5.—Influence of electrolyte concentration on $10^{-1}M$ HCl titration.
—○— without electrolyte —△— $1M$ KCl
—×— $0{\cdot}1M$ KCl —□— $2M$ KCl
—●— $0{\cdot}5M$ KCl —+— $5M$ KCl

The titration curves of sodium, barium and ammonium hydroxides ($0{\cdot}1M$) with $1M$ hydrochloric acid all have much the same shape (Fig. 7), the equivalence point being indicated by a sudden potential jump. The titration curve of $0{\cdot}1M$ potassium hydroxide with $0{\cdot}1N$ sulphuric acid has the normal shape of a potentiometric curve, emphasizing again the influence of the anion.

Table II gives the results of titration of bases, compared with indicator titrations. Potassium hydroxide (down to $10^{-3}M$) can be satisfactorily titrated with hydrochloric acid.

Establishment of the potential

The interface may be considered as a liquid membrane existing between the two phases. The thickness *a* (Fig. 8) of the membrane is determined by layers of molecules of the two liquids fixed

TABLE II.—Titration of $0{\cdot}1N$ bases with $1M$ HCl

Base	Titration, *ml*	
	Interface method	Methyl Red method
NaOH	5·10	5·05
KOH	4·30	4·25
$Ba(OH)_2$	7·20	7·25
NH_4OH	6·50	6·40

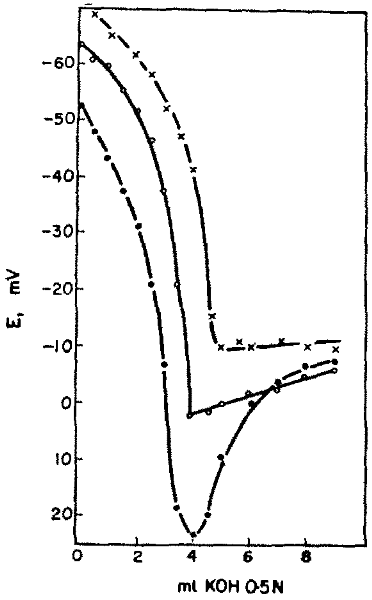


FIG. 6.—Influence of surface-active substances.
—×— surface-active cations
—●— surface-active anions
—○— neutral surface-active

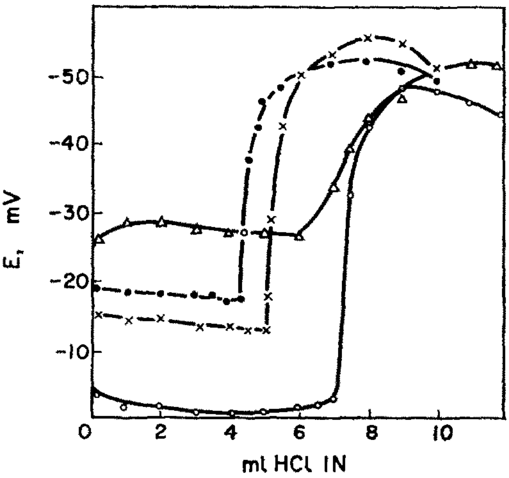


FIG. 7.—Titration curves of bases
—×— NaOH —○— Ba(OH)$_2$
—●— KOH —△— NH$_4$OH

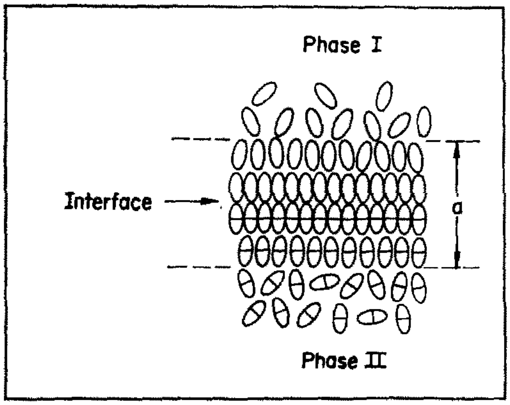


FIG. 8.—Schematic representation of liquid–liquid interface.

mutually by surface tension forces.[2] That is why these molecules cannot move turbulently but only through laminar flow. The potential differences appear owing to differences in activities of the ions on both sides of this membrane. At a proton-sensitive membrane (S) in contact with an electrolyte HX, owing to the distribution of H$^+$ between the solution and the membrane the following equilibrium is established, characterized by the partition coefficient K_{H^+}:

$$H^+_{sol} + S_m \overset{K_{H^+}}{\rightleftharpoons} HS_m^+ \qquad (1)$$

For the interface of the membrane with phase I we can write the expression for the membrane potential:

$$E_{\mathrm{I}} = E_{\mathrm{I}}^{0} + \frac{RT}{F} \ln \frac{(a_{\mathrm{H}^+})_{\mathrm{I}}}{(a_{\mathrm{HS}^+})_{\mathrm{m_I}}} \tag{2}$$

and similarly for the interface with phase II:

$$E_{\mathrm{II}} = E_{\mathrm{II}}^{0} + \frac{RT}{F} \ln \frac{(a_{\mathrm{H}^+})_{\mathrm{II}}}{(a_{\mathrm{HS}^+})_{\mathrm{m_{II}}}} \tag{3}$$

The membrane potential of the system is given by:

$$E_m = E_{\mathrm{I}} - E_{\mathrm{II}} = E_{\mathrm{I}}^{0} - E_{\mathrm{II}}^{0} + \frac{RT}{F} \ln \frac{(a_{\mathrm{H}^+})_{\mathrm{I}}}{(a_{\mathrm{H}^+})_{\mathrm{II}}} - \frac{RT}{F} \ln \frac{(a_{\mathrm{HS}^+})_{\mathrm{m_I}}}{(a_{\mathrm{HS}^+})_{\mathrm{m_{II}}}} \tag{4}$$

Putting $E_{\mathrm{I}}^{0} - E_{\mathrm{II}}^{0} = E^{0'}$ and the diffusion potential

$$E_{\mathrm{d}} = \frac{RT}{F} \ln \frac{(a_{\mathrm{HS}^+})_{\mathrm{m_I}}}{(a_{\mathrm{HS}^+})_{\mathrm{m_{II}}}}$$

we obtain for the membrane potential

$$E_{\mathrm{m}} = E^{0'} - E_{\mathrm{d}} + \frac{RT}{F} \ln \frac{(a_{\mathrm{H}^+})_{\mathrm{I}}}{(a_{\mathrm{H}^+})_{\mathrm{II}}} \tag{5}$$

We observe that the membrane potential will be subject to changes arising from the diffusion potential term E_{d}, as a result of the transfer of ions through the very narrow membrane layer. In other words the hydrogen-ion activity changes in the liquid phase, which can be considered as the internal solution. That is why a linear relationship between E and a_{H^+} holds only in a narrow range of a_{H^+}, which can be observed from the electrode function. With the increase in pH, the shape of the electrode function becomes unusual. This behaviour is reflected in the unusual shape of the titration curves obtained.

At the same time, from equation (5), increase of hydrogen-ion concentration in the n-butanol phase will lower the value of the membrane potential, in accordance with our experimental results. Indeed, previously saturating the n-butanol with $1M$ hydrochloric acid causes a smaller change of potential during the titration of hydrochloric acid with potassium hydroxide. The equivalence point, though distinguishable, is then less certain.

The greater extractibility of sulphuric acid into n-butanol, compared with the other acids titrated,[3] explains the unusual shape of both the electrode function and titration curves for this acid.

Because of the many combinations possible for forming liquid–liquid interface membranes, this type of electrode represents a general form, offering new possibilities for analytical sensors.

Department of Analytical Chemistry
University of Cluj, Cluj, Romania

Candin Liteanu
Maria Mioşcu

Summary—The property that liquid–liquid interfaces modify their electrical charge as a function of the composition of the two phases in contact has been used to detect the end-points in a series of acid–base titrations in the aqueous phase. Although the titration curves are not classical in shape, the equivalence points can be located if the solutions are not too dilute. Good results for concentrations down to $10^{-3}N$ have been obtained. The electrode has a fast response. The influence of surface-active substances on the titration has also been investigated.

Zusammenfassung—Grenzflächen zwischen zwei Flüssigkeiten ändern ihre Ladung in Abhängigkeit von der Zusammensetzung der sich berührenden Phasen. Dieser Effekt wurde zum Nachweis des Endpunktes bei einer Reihe von Säure-Basen-Titrationen in der wäßrigen Phase verwendet. Obwohl die Titrationskurven nicht die klassische Form haben, können die Äquivalenzpunkte bestimmt werden, wenn die Lösungen nicht zu verdünnt sind. Bei Konzentrationen über 10^{-3} N wurden gute Ergebnisse erhalten. Die Elektrode spricht schnell an. Auch der Einfluß oberflächenaktiver Substanzen auf die Titration wurde untersucht.

Résumé—La propriété qu'ont les interfaces liquide–liquide de modifier leur charge électrique en fonction de la composition des deux phases en contact a été utilisée pour déceler les points de fin de dosage dans une série de titrages acide-base en phase aqueuse. Quoique les courbes de titrage ne soient pas classiques dans leur forme, les points d'équivalence peuvent être localisés si les solutions ne sont pas trop diluées. On a obtenu de bons résultats pour les concentrations descendant jusqu'à $10^{-3}N$. L'électrode a une réponse rapide. On a aussi examiné l'influence de substances tensioactives sur le titrage.

REFERENCES

1. F. Haber and Z. Klemensiewicz, *Z. Physik. Chem.*, 1909, **67**, 385.
2. F. M. Fowkes, *J. Phys. Chem.*, 1963, **67**, 2538.
3. Z. Sh. Golynko, D. J. Skorovarov, V. F. Smirnov and N. V. Skvortsov, *Zhr. Prikl. Khim.*, 1965, **38**, 271.

Talanta, 1972, Vol. 19, pp. 894 to 897. Pergamon Press. Printed in Northern Ireland

Studies on nucleation from solution of some analytically important metal chelates—II. Nickel dimethylglyoximate

(*Received* 30 *September* 1971. *Accepted* 26 *November* 1971)

THE LITERATURE on nucleation from solution is filled with experimental results that are inconsistent and confusing. In addition, serious questions are being asked about the validity of the model normally used to interpret experimental data. It seems, then, that progress in the understanding of nucleation from solution is dependent upon improved or entirely new experimental techniques. The aim of this series of investigations is to study the kinetics of crystal nucleation from solution of some analytically important metal chelates, by a diversity of experimental approaches.

In a previous communication[1] a combination of precipitation from homogeneous solution and Vonnegut's droplet technique[2] was used as the experimental method to investigate bis(1,2-cyclohexanedionedioximato) and bis(1,2-cycloheptanedionedioximato)nickel(II) and the corresponding palladium(II) chelates. The present paper describes a direct-mixing and rapid particle-counting technique developed as a second experimental technique for nucleation studies and reports the results found during studies on nickel dimethylglyoximate.

EXPERIMENTAL

Aqueous solutions, one containing dimethylglyoxime and the other nickel(II) were rapidly mixed. Then the number and size distribution of crystals formed during the nucleation and growth periods were determined as a function of time after mixing.

Apparatus

Direct mixing system. Two 10-ml syringes were interlocked so that their plungers operated simultaneously and each was connected to an input port of a Roughton cell. A third syringe was connected to the outlet port of the cell.

Particle-counting system. The rapid particle-counting system was made up of a "Coulter Counter" (Industrial Model B, Coulter Electronics. Industrial Division), a multichannel analyser (Model ND 161F, Nuclear Data Inc.) and a magnetic tape recording unit (Model MT36, Potter Instrument Co. Inc.). The results collected on the magnetic tapes were processed and recovered by computer.

Reagents and solutions

Calibration dispersions for the particle-counting system were prepared in aqueous 1% w/v ammonium chloride solution from polystyrene spheres (Dow Chemical Co.) or ragweed pollen (Coulter Electronic, Industrial Division). Stock solutions of $0.1M$ nickel chloride and $3{\cdot}0 \times 10M^{-3}$ dimethylglyoxime were each prepared in aqueous 1% w/v ammonium chloride solution. Less

Résumé—La propriété qu'ont les interfaces liquide–liquide de modifier leur charge électrique en fonction de la composition des deux phases en contact a été utilisée pour déceler les points de fin de dosage dans une série de titrages acide-base en phase aqueuse. Quoique les courbes de titrage ne soient pas classiques dans leur forme, les points d'équivalence peuvent être localisés si les solutions ne sont pas trop diluées. On a obtenu de bons résultats pour les concentrations descendant jusqu'à $10^{-3}N$. L'électrode a une réponse rapide. On a aussi examiné l'influence de substances tensioactives sur le titrage.

REFERENCES

1. F. Haber and Z. Klemensiewicz, *Z. Physik. Chem.*, 1909, **67**, 385.
2. F. M. Fowkes, *J. Phys. Chem.*, 1963, **67**, 2538.
3. Z. Sh. Golynko, D. J. Skorovarov, V. F. Smirnov and N. V. Skvortsov, *Zhr. Prikl. Khim.*, 1965, **38**, 271.

Talanta, 1972, Vol. 19, pp. 894 to 897. Pergamon Press. Printed in Northern Ireland

Studies on nucleation from solution of some analytically important metal chelates—II. Nickel dimethylglyoximate

(*Received* 30 *September* 1971. *Accepted* 26 *November* 1971)

THE LITERATURE on nucleation from solution is filled with experimental results that are inconsistent and confusing. In addition, serious questions are being asked about the validity of the model normally used to interpret experimental data. It seems, then, that progress in the understanding of nucleation from solution is dependent upon improved or entirely new experimental techniques. The aim of this series of investigations is to study the kinetics of crystal nucleation from solution of some analytically important metal chelates, by a diversity of experimental approaches.

In a previous communication[1] a combination of precipitation from homogeneous solution and Vonnegut's droplet technique[2] was used as the experimental method to investigate bis(1,2-cyclohexanedionedioximato) and bis(1,2-cycloheptanedionedioximato)nickel(II) and the corresponding palladium(II) chelates. The present paper describes a direct-mixing and rapid particle-counting technique developed as a second experimental technique for nucleation studies and reports the results found during studies on nickel dimethylglyoximate.

EXPERIMENTAL

Aqueous solutions, one containing dimethylglyoxime and the other nickel(II) were rapidly mixed. Then the number and size distribution of crystals formed during the nucleation and growth periods were determined as a function of time after mixing.

Apparatus

Direct mixing system. Two 10-ml syringes were interlocked so that their plungers operated simultaneously and each was connected to an input port of a Roughton cell. A third syringe was connected to the outlet port of the cell.

Particle-counting system. The rapid particle-counting system was made up of a "Coulter Counter" (Industrial Model B, Coulter Electronics. Industrial Division), a multichannel analyser (Model ND 161F, Nuclear Data Inc.) and a magnetic tape recording unit (Model MT36, Potter Instrument Co. Inc.). The results collected on the magnetic tapes were processed and recovered by computer.

Reagents and solutions

Calibration dispersions for the particle-counting system were prepared in aqueous 1% w/v ammonium chloride solution from polystyrene spheres (Dow Chemical Co.) or ragweed pollen (Coulter Electronic, Industrial Division). Stock solutions of $0.1M$ nickel chloride and $3{\cdot}0 \times 10M^{-3}$ dimethylglyoxime were each prepared in aqueous 1% w/v ammonium chloride solution. Less concentrated solutions of each were prepared by dilution with aqueous 1% w/v ammonium chloride solution. All solutions were filtered through 0·1-μm PVC membrane filters until each solution gave a negligible background particle-count.

Procedures

Calibrations. For each calibration dispersion and also for mixtures of them the particle counter probe (30-μm aperture) was inserted into 200 ml of the dispersion and the number and size distribution of particles were determined with each of the ten amplification settings of the particle counter; 0·5 ml of the dispersion was used for each measurement. The results from each setting were recorded and stored on magnetic tape.

Nucleation studies. The appropriate nickel solution was placed in one of the 10-ml syringes connected to the Roughton cell and the dimethylglyoxime solution was placed in the second. The solutions were mixed and transferred to the third syringe connected to the cell. After a certain time, a fraction of the contents of the third syringe was transferred to a beaker containing enough 1% w/v ammonium chloride solution to yield 200·0 ml of a dispersion containing about 10^5 countable particles/ml. The number of particles and the size distribution of the particles were determined by the procedure described in the previous paragraph. The reaction conditions for each set of experiments are shown in Table I.

TABLE I.—EXPERIMENTAL CONDITIONS FOR NUCLEATION STUDIES

Electrolyte	Supersaturation	Diluent	Dilution factor	Typical final result, *Counts/ml*
NH_3/NH_4Cl,	$6{\cdot}90 \times 10^2$	NH_3/NH_4Cl,	$4{\cdot}00 \times 10^3$	$3{\cdot}2 \times 10^7$
1% w/v	$4{\cdot}05 \times 10^2$	1% w/v	$2{\cdot}00 \times 10^3$	$10{\cdot}3 \times 10^7$
pH = 7	$2{\cdot}38 \times 10^2$	pH = 7	$2{\cdot}22 \times 10^2$	$2{\cdot}37 \times 10^6$
	$1{\cdot}18 \times 10^2$		$2{\cdot}22 \times 10^2$	$11{\cdot}3 \times 10^6$
	$6{\cdot}91 \times 10^2$		$2{\cdot}00 \times 10^1$	$5{\cdot}40 \times 10^4$

RESULTS AND DISCUSSION

Particle-counting system

Preliminary results with both spherical particles and an actual precipitating system showed that the voltage pulses appearing on the line between the main amplifier and the oscilloscope of the particle counter had those characteristics recommended for best resolution and linearity of the analyser. Also, standard deviations found for equally sized particles compared well with those quoted by the manufacturer. From these results it was concluded that the rapid particle-counting system could be used not only to count the total number of particles above 1 μm in size formed during a nucleation and growth experiment but also to determine the particle-size distribution and its variation. Typical size-distribution curves for nickel dimethylglyoximate are shown in Fig. 1.

Nucleation studies

The total number of particles with a diameter d greater than $2r^*$ at any particular time t after mixing the reagents can be calculated from equation (1).

$$N(2r^*, t) = \int_{2r^*}^{\infty} \left(\frac{\partial N(d, t)}{\partial d}\right)_t \mathrm{d}d \qquad (1)$$

where r^* = the critical radius of the nucleus.

Further, the rate of nucleation J is defined as $\partial N(2r^*, t)/\partial t$. Therefore, the slope of a plot of $N(2r^*, t)$ *vs* time is the rate of nucleation for any given set of reation conditions. Because the particle counter had a sensitivity limit of about 1 μm the lower limit of integration in equation (1) was changed from $2r^*$ to 1 μm and $N(2r^*, t)$ was replaced by $N(1, t)$ in all of the data analyses. Typical plot of $N(1, t)$ *vs.* time constructed from the data from Fig. 1, are shown in Fig. 2. The rate of nucleation was found to be proportional to $(\log s)^{-2}$.

That the rates of nucleation reported here are rates of homogeneous nucleation was indicated by the following general characteristics noted during comparative study of about 150 size distribution curves. In all but the very early size-distributions at any one initial supersaturation a large maximum with a small shoulder on the large-particle side was observed. With increased initial supersaturation there was a marked increase in the total number and a decrease in the average size of the particles formed. In addition, the experimental values of J and S conformed to the correlation drawn from

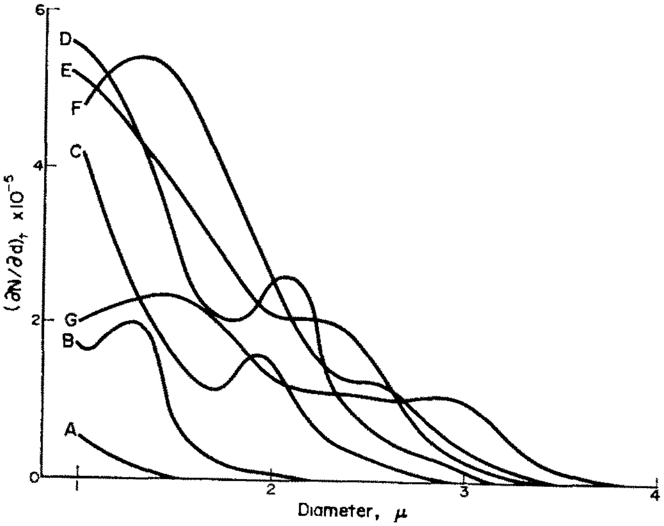


FIG. 1—Nickel dimethylglyoxinate size distributions ($C_0 = 2{\cdot}5 \times 10^{-4}M$). Size distributions A, B, C, D, E, F and G taken after 10, 30, 38, 60, 90, 120 and 230 sec. respectively

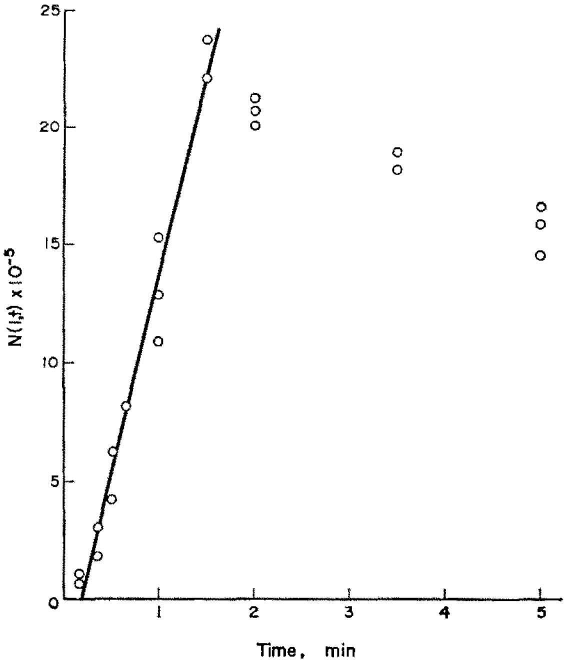


FIG. 2—Variation of the total number of nickel dimethylglyoximate crystals formed (above 1μ) with time. ($C_0 = 2{\cdot}5 \times 10^{-4}M$).

the Volmer-Weber, Becker-Döring model of homogeneous nucleation of crystals from solution. Recent criticism of the model, however, does cast doubt on the validity of the predicted correlation.[3,4,5]

Various parameters in the model calculated from the slope and intercept of the correlation of nucleation rate with supersaturation are shown in Table II. Although their actual significance is unclear, we find that these parameters do provide an adequate means of comparing experimental results. Experimental values of the kinetic constant A many orders of magnitude smaller than the

TABLE II.—VALUES OF VARIOUS PARAMETERS FOR NICKEL DIMETHYLGLYOXIMATE

Molecular volume in the solid phase, cm^3	Log A(†)	S^+(‡)	Shape factor	Interfacial energy, erg/cm^2	r^+(§) nm	n^+(§)
$2{\cdot}97 \times 10^{-22}$	9·4	77	109	13	—	12
			$16\pi/3$	24	4·4	

† Log A calculated theoretically ~ 27.
‡ S^+ = the value of S, the initial supersaturation when $J = 1$.
§ The value of r^* or n^*, the number of molecules in the critical nucleus, when $S = S^+$.

calculated value have been reported previously for other metal chelates,[1,6] other molecular compounds[7,8] and for ionic salts.[9] Discussions of this discrepancy have appeared elsewhere.[1,7,8,9]

Acknowledgement—The authors acknowledge the financial assistance provided by the National Research Council of Canada.

Department of Chemistry
McMaster University
Hamilton, Ontario,
Canada

J. D. HANNA
O. E. HILEMAN JR.®

Summary—A new direct-mixing and rapid particle-counting system useful for studies on crystal nucleation solution is described. The methods used to calibrate and evaluate the system are reported together with the results obtained during studies on nucleation from solution of nickel dimethylglyoximate. The Volmer-Weber, Becker-Döring model of the nucleation process is used to correlate the results.

Zusammenfassung—Ein neues schnelles Teilchenzählsystem mit direkter Mischung wird beschrieben, das für Untersuchungen über die Kristallkeimbildung aus Lösungen von Nutzen ist. Es wird über die Methoden berichtet, mit denen das System geeicht und überprüft wurde, sowie über die Ergebnisse von Keimbildungsuntersuchungen aus Lösungen von Nickeldimethylglyoximat. Das Keimbildungsmodell von Volmer-Weber und Bekker-Doring wird verwendet, um die Ergebnisse zu ordnen.

Résumé—On décrit un nouveau système de mélange direct et de comptage de particules rapide, utile pour les études sur la production de germes cristallins en solution. On rapporte les méthodes utilisées pour étalonner et évaluer le système, en même temps que les résultats obtenus pendant les études sur la nucléation d'une solution de diméthylglyoximate de nickel. On utilise le modèle Volmer–Weber, Becker–Doring du processus de nucléation pour coordonner les résultats.

REFERENCES

1. J. A. Velazques and O. E. Hileman, Jr., *Talanta*, 1970, **17**, 623.
2. B. Vonnegut, *J. Colloid. Sci.*, 1948, **3**, 563.
3. F. Abraham, *J. Chem. Phys.*, 1969, **50**, 3977.
4. E. R. Buckle, *Trans. Faraday. Soc.*, 1969, **65**, 1267.
5. F. L. Binsbergen, *Kolloid-Z.* 1970, **237**, 289.
6. J. D. Hanna and O. E. Hileman, unpublished work.
7. W. J. Dunning and N. T. Notely, *Z. Electrochem.*, 1957, **61**, 55.
8. W. J. Dunning and A. J. Shipman, *Proc. Agric. Ind. Tenth Int. Congr., Madrid*, 1954.
9. J. A Velazques and O. E. Hileman, Jr., *Can. J. Chem.*, 1970, **48**, 2896.

Talanta, 1972, Vol. 19, pp. 899 to 902. Pergamon Press. Printed in Northern Ireland

ANNOTATION

Losses of iridium during heating in various atmospheres

(*Received* 31 *August* 1971. *Accepted* 24 *October* 1971)

THE LOSS of iridium on heating may present a serious difficulty in analysis. Although it has been reported[1] that there are significant losses of iridium when the finely divided metal is heated in air at 800–950°, there has been no extensive, systematic investigation of this problem.

The reaction of iridium metal with oxygen[2–5] and with chlorine[1,6] has been investigated by several authors, most of whom studied the rates of reaction at relatively high temperatures, and used large quantities of material. The oxidation of the platinum metals was surveyed by Chaston[3] and indicates the surface formation of the oxide but no appreciable loss in weight of iridium up to 900°. Other authors[2,4] using mg or g amounts of iridium found weight losses in air of about 1–30 μg/mm^2/hr for the temperature range 650–1400°. Iridium losses during fire assay and cupellation were reported[7] to be as high as 63% after cupellation for 90 min at 1300°; radioactive iridium was used as a tracer. Beamish[1] reports losses of 1–3% on heating mg amounts of iridium in air at 800–950° and also notes complete chlorination of the metal and some volatilization when chlorine and sodium chloride are used at 700° for 8 hr. Some authors[6,8] have studied the chlorination as a preparative method for the various halides but these again deal with mg amounts and temperatures above 600°. Other reports concern the conversion of iridium compounds when various gases are used.[8–12] Delépine[10,11] reported on the use of sodium chloride and caesium chloride in aiding the action of chlorine on g amounts of iridium metal at 600°. Krauss and Gerlach investigated the products of the reaction of iridium metal with chlorine and with a mixture of chlorine and carbon monoxide at 600–620°. Merinis and Bouissières[13] used chlorination to volatilize submicrogram amounts of radioactive iridium at 700–1000° and used this technique as a means of separating different elements. The products were condensed in a tube possessing a large fixed temperature gradient; iridium moved 0·10–0·24 m and condensed in an area at about 575° in temperature.

The present report describes the effect of various atmospheres on iridium, both mg and μg amounts of metal and a wide range of temperatures being used.

EXPERIMENTAL

Apparatus

Lindberg Hevi-Duty Tube furnace.
Baird-Atomic Spectrometer Model 530.
Ultra Violet Products U.V. lamp, Model PCQX1.
Vycor combustion tubes 25 mm × 0·75 m and boats 10 × 40 mm.
Iridium-192 from Amersham/Searle.

Procedure

The volatility of iridium metal in various atmospheres was studied by using ^{192}Ir as a radioactive tracer because of its convenient 74·4 day half-life. The iridium samples were prepared by evaporating aliquots of the tracer in a Vycor combustion boat with or without the addition of various amounts of inactive iridium. The residue was then reduced to metal by heating the boat in a hydrogen atmosphere at 600–700° for 4 hr and then allowing it to cool in hydrogen.

Various sources were used to provide the different atmospheres tested. Commercial gas cylinders were used for hydrogen, nitrogen, oxygen, hydrogen sulphide, hydrogen chloride and chlorine. Air was obtained from an air-compressor. Bromine was obtained by gentle heating of a flask containing bromine, which was directly connected to the combustion tube. Hydrochloric and hydrobromic acids were obtained by boiling the acids. Hydrobromic acid, hydrochloric acid, acetic acid and perchloric acid atmospheres were obtained by bubbling air or oxygen or chlorine through a 500-ml flask half-filled with the particular acid and leading *via* Tygon tubing to the combustion tube. The gas flow for the system was controlled at between 2–5 ml/min in all cases.

The physical arrangement was as shown in Fig. 1 with both the combustion boat and tube offset in the furnace. The boat was situated closer to the gas inlet end and the tube had a longer outlet than inlet to aid in condensing any volatile compounds. The outlet from the combustion tube was led through a water trap to collect any volatiles and then to the fume exhaust. When perchloric acid was used, an all-glass system was employed with dry ground-glass joints fitted to a Vycor combustion tube.

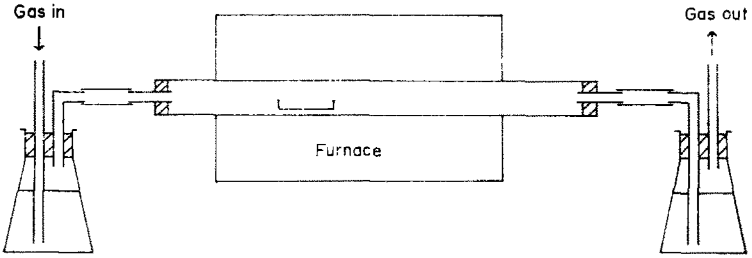


FIG. 1.—Apparatus used.

The distribution of ^{192}Ir radioactivity was observed by spectrometer with a 75-mm NaI(Tl) crystal with an additional lead shield fitted so that only an area 30 × 60 mm was counted. The change in ^{192}Ir distribution was observed by counting the tube before and after every run at a given temperature in a particular atmosphere. The same iridium sample was used until the change in distribution became significant. A count was taken at positions along the tube of 5, 15, 20, 25, 30, 35, 40, 50, 60, 70 cm, measured from the inlet end. The combustion boat was centred at 25 cm with the ends of the furnace at about 15 and 49 cm. In one case a low-pressure mercury lamp was used to irradiate the chlorine gas before it passed over the sample.

RESULTS AND DISCUSSION

The results from several trials using various amounts of iridium, various atmospheres and various temperatures are reported in Table 1. It should be noted that in no case was any radioactivity observed in the water trap for the effluent gases. When a volatile compound was produced, iridium

TABLE I.—VOLATILITY OF Ir IN VARIOUS ATMOSPHERES

Gas	Wt. of Ir	Temp., *°C*	Time, *hr*	Loss from boat, %	Observation
H_2	5·3 mg	460–860	20	0	
		900	46	0	
	50 μg	540–980	24	0	
N_2	5·3 mg	550–900	20	0	
	50 μg	580–1000	24	0	
O_2	5·3 mg	490	20	0	
		650	20	trace	
		760	20	10	Black residue in tube
		880	20	90	
		910	20	99·5	
	5·3 mg	370–570	96	0	
		590–650	96	5	
		690	96	10	Black-green deposit in tube.
		750	96	25	
		800	144	50	
	50 μg	540	24	20	
		630	24	30	
		680	24	50	
		750	24	60	
		880	24	66	
		930	24	90	
	50 μg	160–280	96	0	
		400	96	?	
		440	96	20	
		460	96	28	
		500	96	29	
Cl_2	5·3 mg	120–480	24	0	
		600	24	4	pink deposit
		700	24	70	dark red deposit
		840	24	97	black, red and yellow deposits

TABLE I. (*Continued*)

Gas	Wt. of Ir	Temp., °C	Time, *hr*	Loss from boat, %	Observation
	5·3 mg	280	24	0	
		410	24	50	green-black deposit
	50 μg	100–160	24	0	
		220	24	10	
		290	24	33	
		370	24	50	
		500	24	94	
	50 μg +	100–160	24	0	
	300 mg NaCl				
		205	24	?	boat tinged with red
		260	24	8	
		310	24	40	
		380	24	84	
	50 μg +	140–200	24	0	
	500 mg NaCl added				
	as solution and	240	24	10	
	evaporated	340	24	60	
		400	24	73	
Cl_2	10^{-13}g*	110–230	24	0	
(irradiated		440	24	15	
with mercury lamp)		540	24	25	
Br_2	50 μg	100–410	24	0	blue tinge to boat at 340°
HCl	50 μg	440–540	24	0	
(cylinder)		610	24	10	
		710	24	70	pink deposit in tube
HCl	50 μg	100–390	24	0	
(boiling acid)		460	24	5	
		540	24	95	yellow deposit in tube
		640	24	99·5	
HCl	50 μg	140–290	24	0	
(air through acid)		380	24	25	
	2 mg	220–320	24	0	
		390	24	4	
		500	24	12	pink deposit in tube
HCl	50 μg	240–300	24	0	
(O_2 through acid)					
		410	24	25	
HBr	50 μg	150	24	0	
(boiling acid)		250	24	?	
		380	24	12	
		440	24	16	
		560	24	40	boat material is red
		700	24	93	
HBr	50 μg	150–310	24	0	
(air through acid)		460	24	11	
HBr	50 μg	300	24	0	
(O_2 through acid)		450	24	5	
		550	24	10	
H_2S	50 μg	140–640	24	0	
		740	24	30	
CH_3COOH	50 μg	190–700	24	0	
(air through acid)		800	24	15	
$HClO_4$	10^{-13}g*	110–590	24	0	
(air through acid)					
$HClO_4$ + Cl	10^{-13}g*	100	24	0	
($Cl_2{}^4$ through acid)		200	24	3	

* Radioactive ^{192}Ir only.

activity moved in both directions in the combustion tube, condensing just outside the furnace area, although the majority of the activity was found at the down-stream position. No attempt was made to identify the volatile species because of the difficulty of analysis of the vapour and the probability of a difference in either the condensed product or the dissolved product.

The results indicate that only in nitrogen or hydrogen may iridium be heated to much above 700° without some loss. In other atmospheres iridium losses occurred to a varying extent, depending on the amount of material present and probably on its surface area. In most experiments where air or oxygen was bubbled through acid, the acid did not have a significant effect on the temperature at which volatilization occurred although the species formed may well be different. In these cases, significant movement of iridium activity was observed at about 400°, which is similar to the experiments using oxygen alone. In chlorine, iridium was volatilized at temperatures as low as 220° and this was not affected by the presence of sodium chloride or by the chlorine being passed through perchloric acid. Microamounts seem to be more affected at the lower temperatures in chlorine and while this may not be of importance in many analyses, it may be useful for the separation of micro- and submicro-amounts of radioisotopes, *etc.*

The results obtained indicate that iridium should not be treated as an inert metal in analysis but that due concern should be paid to losses that may occur during heating, especially in chlorine or oxygen atmospheres.

Acknowledgement—The author wishes to thank the National Research Council of Canada for its financial support and Johnson Matthey and Mallory Ltd. (Toronto Canada) for providing the iridium used.

Department of Chemistry
University of Manitoba
Winnipeg 19, *Manitoba, Canada*

A. CHOW

Summary—The volatility of iridium metal in different atmospheres was studied, using various weights, times and temperatures. Significant volatility was observed in oxygen and oxygen plus acid at temperatures above 400° and in chlorine above 220°

Zusammenfassung—Die Flüchtigkeit von metallischem Iridium in verschiedenen Atmosphären wurde bei verschiedenen Gewichten, Zeiten und Temperaturen untersucht. Merkliche Flüchtigkeit wurde in Sauerstoff und in Sauerstoff plus Säure bei Temperaturen über 400° beobachtet, in Chlor über 220°.

Résumé—On a étudié la volatilité de l'iridium métallique dans différentes atmosphères, en utilisant des poids, des temps et des températures divers. On a observé une volatilité importante en oxygène et oxygène plus acide aux températures supérieures à 400° et en chlore au-dessus de 200°.

REFERENCES

1. M. A. Hill and F. E. Beamish, *Anal. Chem.*, 1950, **22**, 590.
2. C. A. Krier and R. I. Jaffee, *J. Less-Common Metals*, 1963, **5**, 411.
3. J. C. Chaston, *Platinum Metals Rev.*, 1965, **9**, 51.
4. W. L. Phillips Jr., *Am. Soc. Metals, Trans. Quart.*, 1964, **57**, 33.
5. W. Betteridge and D. W. Rhys, *Intern. Congr. Metallic Corrosion* 1*st*, *London*, 1961, 186.
6. B. D. Stepin and A. I. Chernyak, *Zh. Neorgan. Khim.*, 1960, **5**, 2157.
7. T. W. Steel, *National Inst. Metallurgy S. Afr. Rept.* No. 890.
8. L. Wohler and S. Streicher, *Ber.*, 1913, **46**, 1577.
9. M. Delépine, *Compt. Rend.*, 1914, **158**, 264.
10. *Idem*, *Bull. Soc. Chim. France*, 1939, 1471.
11. *Idem*, *ibid.*, 1956, 282.
12. F. Krauss and H. Gerlach, *Z. Anorg. Allgem. Chem.*, 1925, **147**, 265.
13. J. Merinis and G. Bouissières, *Anal. Chim. Acta*, 1961, **25**, 498.

Talanta, 1972, Vol. 19, pp. 903 to 914. Pergamon Press. Printed in Northern Ireland

EINE SÄULENCHROMATOGRAPHISCHE METHODE DER MOLYBDÄNMATRIX-ABTRENNUNG ZUR BESTIMMUNG VON ALKALI- UND ERDALKALI-SPUREN IN MOLYBDÄN UND MOLYBDÄNVERBINDUNGEN

S. KARAJANNIS, H. M. ORTNER und H. SPITZY
Institut für Allgemeine Chemie, Mikro- und Radiochemie, Technische Hochschule Graz, Technikerstraße 4, A-8010 Graz und Metallwerk Plansee AG. & Co. KG., A-6600 Reutte, Österreich

(*Eingegangen am* 14. *Oktober* 1971. *Angenommen am* 5. *Dezember* 1971)

Zusammenfassung—Eine neue, säulenchromatographische Methode der Molybdän-Matrixabtrennung bei der Alkali- und Erdalkali-Spurenbestimmung wird beschrieben. Die Molybdän-Sorption gelingt auf Sephadex G-10 Säulen bei pH 2,5 in ammoniumchloridhaltiger Lösung durch Ausbildung eines Molybdän-Ammoniak-Glucose-komplexes. Die quantitativ im Eluat verbleibenden Alkalispuren werden mittels Flammenemissionsphotometrie, die Erdalkalispuren mittels Atomabsorption erfaßt. Bei einer Trenndauer von 2 Stunden und entsprechender Automatisierung ist das Verfahren für die routinemäßige Alkali- und Erdalkali-Spurenanalyse in metallischem Molybdän, MoS_2, MoO_3, MoO_2 etc. geeignet. Die relative Standardabweichung liegt bis 60 ppm bei ±10%, darüber bei ±5%.

ALKALI- und Erdalkali-Verunreinigungen bzw. Beimengungen spielen bei der Molybdänherstellung eine Rolle, da sie die Eigenschaften des Endproduktes beeinflussen können. Diesbezügliche systematische Untersuchungen existieren jedoch noch nicht, was nicht zuletzt darauf zurückzuführen sein dürfte, daß die bekannten Methoden der exakten Bestimmung von Alkali- and Erdalkalispuren in Molybdän sehr mühsam, kontaminationsanfällig und aufwendig sind. Sublimationsverfahren zur Matrixbeseitigung[1] sind bei Molybdän schlecht reproduzierbar. Ionenaustauschverfahren,[2,3] insbesondere zur Alkaliabtrennung ergeben auf Grund schwer zu reinigender Reagenzien hohe Blindwerte oder machen langwierige Reinigungsoperationen derselben nötig. Über die direkte Bestimmung von Alkali- und Erdalkalispuren in Molybdän mittels physikalisch-chemischer Analysenverfahren wie Festkörpermassenspektrometrie, Emissionsspektralanalyse, Aktivierungsanalyse oder Atomabsorption ist wenig bekannt.[4,5] Durchwegs beeinträchtigen ausgeprägte Matrixeffekte die Reproduzierbarkeit und Nachweisempfindlichkeit der Messung. Insbesondere bei der Analyse von Molybdänoxiden führt die überaus stark ausgeprägte Inhomogenität dieser Materialien beim Einsatz kleiner Probenmengen (Massenspektrometrie, Emissionsspektralanalyse) zu stark streuenden Werten.

Die ausgeprägte Tendenz des Molybdäns zur Komplexbildung mit aliphatischen Polyhydroxoverbindungen ist schon seit längerem bekannt. Es war daher zu erwarten, daß Molybdän auch von Dextrangelen stark sorbiert wird. Ferner ist bekannt, daß Alkali- und Erdalkaliionen sowie eine Vielzahl anderer Anionen und Kationen bei Ionenstärken über 0,01 Sephadexsäulen ungehindert passieren. Somit schien die Abtrennung des Molybdäns als Matrix von einer unter Umständen beträchtlichen Anzahl von Spurenenlementen gegeben. Auf Grund dieser Überlegungen wurde zunächst das Verhalten von Molybdän an Dextrangelen prinzipiell untersucht.

Hierauf gelang auf Sephadex G-10 die Ausarbeitung einer raschen und sicheren Abtrennung von Alkali- und Erdalkalispuren von Molybdän. Dieses säulenchromatographische Verfahren bedient sich lediglich der durch Isothermdiffusion in beinahe beliebiger Reinheit leicht zu erhaltenden Reagenzien Ammoniak und Salzsäure. Bei einer Trenndauer von 2 Stunden und entsprechender Automatisierung ist das Verfahren für die routinemäßige Alkali- und Erdalkalispurenanalyse in Molybdän bestens geeignet.

AUSARBEITUNG DER METHODE

Geräte

Radioaktivitätsmessungen erfolgten mit einem Zählgerät der Firma Frieseke & Hoepfner, FH 49A, Grundsonde FH 421 AS, NaJ-Bohrlochszintillationskristall Z 11, in Verbindung mit einem 100-Kanal Gammaspektrometer TMC-Gammascope II[*] in Einkanalschaltung.

Flammenemissionsspektrophotometrische und atomabsorptionsphotometrische Messungen wurden an folgenden Geräten durchgeführt: Zeiss-Spektralphotometer PMQ II mit den Flammenzusätzen FA1 und FA2; Eppendorf Flammenphotometer[†]; Perkin–Elmer Atomabsorptionsspektrophotometer 290B[†]; Beckmann DU[‡]; Jarrel Ash Atomsorb, Serie 82–250.[‡]

Säulenchromatographie: Es kamen sowohl käufliche Säulen (Pharmacia, Uppsala, Schweden: Typen K9/15 und K15/30) als auch selbst gefertigte Säulen zum Einsatz. Letztere wurden aus Plexiglasrohren (30 mm Durchmesser), gestanzten Filterplatten aus Hochdruckpolyäthylen (Plastibrand-Labpor, Dicke 1,6 mm, Porosität 70 μm) und Auslauftrichtern aus Vinidur hergestellt. Proben- und Elutionsmittelaufgabe erfolgte mit einer Mikropumpe der Firma Bühler & Co., Tübingen, BRD Typ mp 1. Es wurden ausschließlich Silikonschläuche verwendet. Ein automatischer Fraktionssammler "Fraktomat", Buchler Instruments, Fort Lee, USA, wurde bei Bedarf eingesetzt. Es wurde durchwegs in PVC-, Polyäthylen- bzw. Teflongefäßen gearbeitet.

Materialien

Sephadex G-10 fine, G-15 fine und LH-20 fine von Pharmacia, Uppsala.

Natriumchlorid, Kaliumchlorid, Cäsiumchlorid, Ammoniumchlorid, Calciumchlorid-4-hydrat, Ammoniaklösung (min. 25 %), Salzsäure (min. 37 %), Salpetersäure (min. 65 %), alle Reinheitsgrad "suprapur", sowie Magnesiumchlorid, Zinn(II)chlorid, Kaliumthiocyanat p.a. und Äthylendiamintetraessigsäure (Titriplex II), von Merck, Darmstadt.

MoO$_3$, zweifach sublimiert, von Metallwerk Plansee AG. & Co. KG.

^{22}Na und ^{47}Ca von The Radiochemical Centre, Amersham, England.

^{99}Mo und ^{42}K wurden durch Bestrahlung von MoO$_3$ bzw. KCl im ASTRA-Reaktor der Österreichischen Studiengesellschaft für Atomenergie in Seibersdorf selbst hergestellt.[§]

Bidestilliertes Wasser aus einer Quarzapparatur.

Die Sorption von Molybdän(VI) *an Dextrangelen*

Erste Versuche wurden unter dynamischen Bedingungen, d.h. auf Säulen durchgeführt, Tab. I. Das am engsten vernetzte Gel Sephadex G-10 weist die größte Sorptionskapazität für Molybdän auf. Daher wurden sämtliche weiteren Versuche mit diesem Gel durchgeführt.

In einer Reihe von Batch-Versuchen, Tab. II, wurde das Verhalten von Mo(VI)-Lösungen auf Sephadex G-10 einer näheren Untersuchung unterzogen. Es wurde 0,5 g trockenes Sephadex G-10 in ein Zentrifugenglas eingewogen und 3 ml Wasser

---

[*] Das Gerät wurde vom Österreichischen Fonds zur Förderung der wissenschaftlichen Forschung zur Verfügung gestellt.

[†] Für die Ermöglichung von Messungen an diesen Geräten sei Herrn Dipl. Ing. Dr. techn. H. Lapaine, Leiter der Landwirtschaftlich-chemischen Bundesversuchs- und Untersuchungsanstalt der Steiermark, herzlich gedankt.

[‡] Für die Ermöglichung von Messungen an diesen Geräten sei Herrn Doz. Dr. E. Schnell, Institut für Anorganische und Analyt. Chemie der Universität Innsbruck (Vorstand Prof. Dr. E. Hayek) herzlich gedankt.

[§] Dem Leiter des Chemieinstitutes des Reaktorzentrums Seibersdorf, Herrn Dr. H. Bildstein, sei für die Erlaubnis zur Durchführung dieser Arbeiten gedankt.

TABELLE I.—DURCHBRUCHSKAPAZITÄTEN FÜR EINIGE SEPHADEXGELE

Typ	Durchbruchskapazität in *mg* Mo/*ml* Säulenvolumen
Sephadex G-10	83
Sephadex G-15	58 (70% bezogen auf Sephadex G-10)
Sephadex LH-20	50 (60% bezogen auf Sephadex G-10)

Versuchsparameter: Säulendimensionen: 125 × 9 mm
Bettvolumen: 8 ml; Durchflußgeschwindigkeit: 0,235 ml.h^{-1} mm^{-2}
Aufgabelösung: 0,14*M* Mo-Lösung, mit HCl auf pH 2,5 gestellt.
Zimmertemperatur.

TABELLE II.—ÜBERSICHT ÜBER BATCH-VERSUCHE ZUM SORPTIONSVERHALTEN DES MOLYBDÄNS AN SEPHADEX G-10

	Eingesetzte Mo-Menge, *mmol*	Schüttelzeit, *min*	pH-Wert vor Batch-Versuch	pH-Wert nach Batch-Versuch	Eingesetzte NH_4Cl-Menge, *mmol*	% Mo sorbiert	D_G
(a)	0,3	30	2,7	—	0,1	51	12,5
	0,3	60	2,7	—	0,1	55	14,7
	0,3	120	2,7	—	0,1	57	15,9
(b)	0,3	60	1,1	—	0,1	69	26,7
	0,3	60	1,4	—	0,1	86	73,7
	0,3	60	1,7	—	0,1	86	73,7
	0,3	60	2,2	2,4	0,1	69	26,7
	0,3	60	2,7	3,2	0,1	55	14,7
	0,3	60	3,2	3,6	0,1	48	11,1
	0,3	60	4,1	4,5	0,1	27	4,4
	0,3	60	5,0	5,0	0,1	9	1,2
(c)	0,3	60	1,6	—	0,1	86	73,7
	0,03	60	1,6	—	0,01	80	48,0
	0,003	60	1,6	—	0,001	78	42,5
	0,0003	60	1,6	—	0,0001	73	32,4
(d)	0,52	60	2,5	3,0	0,561	70	28,0
	0,30	60	2,5	3,0	0,561	79	45,1
	0,03	60	2,5	3,0	0,561	91	121,3
	0,003	60	2,5	2,8	0,561	90	108,0
	0,0003	60	2,5	2,6	0,561	89	97,1
(e)	0,3	60	2,5	3,0	0,561	79	45,1
	0,3	60	3,0	3,8	0,561	70	28,0
	0,3	60	3,4	4,2	0,561	58	16,6
(f)	0,522	60	2,5	3,0	0,0	46	10,2
	0,522	60	2,5	3,0	0,3	60	17,9
	0,522	60	2,5	3,1	0,561	70	28,0
	0,522	60	2,5	3,1	1,122	80	48,2

zugesetzt. Das Gel wurde über Nacht quellen gelassen. Hierauf wurden jeweils 3 ml der zu untersuchenden Lösung zugesetzt und auf einer Schüttelmaschine kräftig geschüttelt. Die Lösungen waren durchwegs mit ^{99}Mo* dotiert. Drei ml der überstehenden Lösung wurden nach Zentrifugieren vorsichtig abpipettiert und die Impulsrate im Bohrlochszintillationszähler gemessen. Anschließend wurde nochmals der pH-Wert gemessen. Sämtliche Batch-Versuche wurden bei Zimmertemperatur

---

* ^{99}Mo wurde ab 0,30 MeV integral gemessen.

ausgeführt (*ca.* 22°C). Die Berechnung der Gewichtsverteilungskoeffizienten erfolgte nach folgender Gleichung:

$$D_g = \frac{\text{mmol sorbiertes Mo/g trockenes Gel}}{\text{mmol Mo/ml Lösung}}$$

Bei den Batch-Versuchen konnte folgendes festgestellt werden.

(*a*) *Kinetik.* Die Ausbildung des Molybdän-Sephadexkomplexes verläuft bei Zimmertemperatur relativ langsam. Daher muß bei Säulenexperimenten mit ziemlich niedrigen Durchflußgeschwindigkeiten gearbeitet werden.

(*b*) *pH-Abhängigkeit.* Die Molybdän-Sorption ist sehr pH-abhängig und weist in Lösungen mit geringer Fremdsalzkonzentration ein ausgeprägtes Optimum bei pH 1,4–1,7 auf. Der pH-Wert nach dem Batch-Versuch liegt durchwegs höher als vorher.

(*c*) *Abhängigkeit von der Molybdän-Konzentration.* Überraschenderweise nahmen die Verteilungskoeffizienten mit abnehmender Mo(VI)-Konzentration ab. Die zweite Variable dieser Versuchsreihe war die ebenfalls sinkende NH_4Cl-Konzentration. Es lag daher nahe, das Experiment bei konstanter NH_4Cl-Konzentration zu wiederholen.

(*d*) *Abhängigkeit von der Ammoniumchloridkonzentration.* Tatsächlich ist die Molybdän-Sorption nicht nur eine Funktion des pH-Wertes, sondern auch der NH_4Cl-Konzentration. Bei konstanter Ammoniumchloridkonzentration erreicht die Molybdän-Sorption bei mittleren Molybdän-Konzentrationen ein Maximum. Die sinkende Sorption bei niedriger Molybdän-Konzentration läßt auf eine gewisse Löslichkeit des anzunehmenden Mo–NH_3-Glucosekomplexes schließen. Dies steht auch in Einklang mit den unter (*c*) beschriebenen Resultaten.

(*e*) *pH-Optimum bei Molybdän-Sorption in Gegenwart von* NH_4Cl. Der pH-Variation sind bei hoher Molybdän- *und* NH_4Cl-Konzentration Grenzen gesetzt. Zu niedrige pH-Werte verursachen vor allem bei längerem Stehen der Lösung eine (ziemlich temperaturabhängige) Ausfällung von Ammoniummolybdat. pH-Werte unter 2,5 können daher nicht verifiziert werden. Wieder zeigt sich ein deutliches Absinken der Sorption mit steigendem pH-Wert.

(*f*) *Endgültige Optimierung.* Schließlich wurde bei pH 2,5 nochmals der Einfluß steigender Ammoniumchloridmengen bei höchstmöglicher Molybdän-Konzentration untersucht. Die eingesetzte Molybdänlösung (0,174*M*) entspricht der für spätere Säulenexperimente verwendeten Einwaage von 2,5 g Mo/100 ml.

Säulenchromatographie

Weitere Versuche wurden wieder unter dynamischen Bedingungen in einer Reihe von Säulenexperimenten unternommen. Die Füllung der Säulen wurde nach der in der Gelchromatographie üblichen Art vorgenommen. Wichtig ist eine Einlaufzeit von mindestens 12 Stunden bei *ca.* 100 ml/h nach erfolgter Neufüllung einer Säule. Zur Feststellung der Molybdändurchbruchskapazität wurde die Tüpfelreaktion mit $SnCl_2$ und KSCN angewandt.[6]

Abbildung 1 zeigt ein überaus stark ausgeprägtes pH-Optimum für die Molybdändurchbruchskapazität bei pH 2,5. Dies steht in Einklang mit den Batch-Versuchen. Abbildung 2 zeigt pH-Profile von Eluaten bei Säulen experimenten, welche unter sonst gleichen Bedingungen mit verschiedener NH_4Cl-Konzentration der

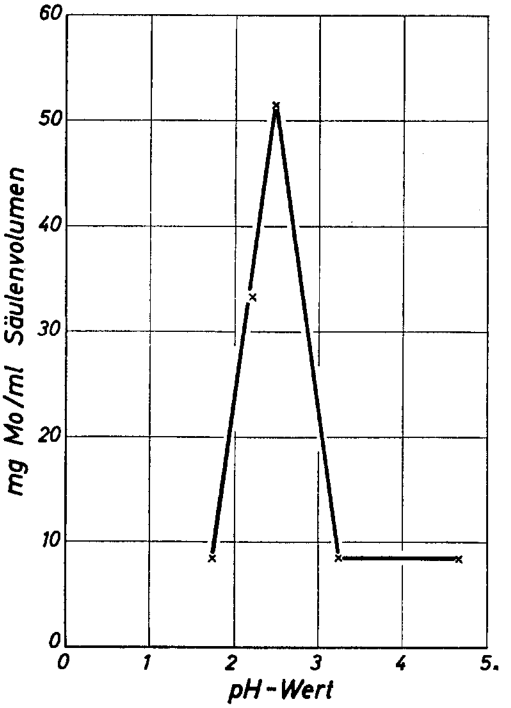


ABB. 1.—Bestimmung der Mo-Durchbruchskapazität auf Sephadex G-10 Säulen als Funktion des pH-Wertes.

Säulendimensionen: 125 × 9 mm; Zimmertemperatur; Durchflußgeschwindigkeit: 0,47 ml/h^{-1} mm^{-2} (= 30 ml/h); Aufgabelösung: 0,14*M* Mo; 0,05*M* NH$_4$Cl. pH-Einstellung jeweils mit HCl.

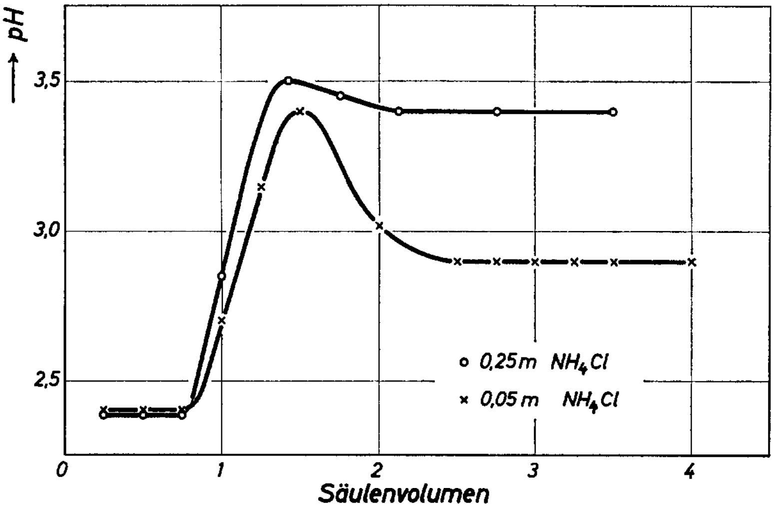


ABB. 2.—pH-Elutionsprofile bei Molybdänsorption auf Sephadex G-10 Säulen. Einfluß steigender Ammonchloridmengen.

Säulendimensionen: 100 × 30 mm; Zimmertemperatur; Durchflußgeschwindigkeit: 0,14 ml/h^{-1} mm^{-2}; Aufgabelösung: 0,174*M* Mo; pH-Wert 2,5.

Aufgabelösung durchgeführt wurden. Bei Komplexbildung des Molybdäns mit den Glucoseeinheiten des Dextrangels werden OH-Ionen frei. Bei höherer NH_4Cl-Konzentration ist diese OH-Ionenbildung offensichtlich verstärkt; dies deutet wohl auf ausgeprägtere Komplexbildung bei Anwesenheit von NH_4Cl hin. Auch bei den Batch-Experimenten läßt sich diese Tendenz feststellen. Da durch die auftretende pH-Änderung ein Abweichen von dem zur Komplexbildung optimalen pH-Wert eintritt, wurde versucht, letzteren durch Anwendung eines geeigneten Puffergemisches konstant zu halten. Sämtliche in Frage kommenden Puffergemische enthalten jedoch organische Säureanionen, die mit Molybdän Komplexe bilden. Es kommt dadurch immer zu einer Verminderung der Durchbruchskapazität. Daher wurde auf eine Pufferung der Aufgabelösung verzichtet.

Wie schon die Batch-Experimente zeigten, muß mit ziemlich niedrigen Durchflußgeschwindigkeiten gearbeitet werden. Bis zu 20 $ml.h^{-1}.cm^{-2}$ erreicht man jedoch Säulenkapazitäten, die mit denen von Ionenaustauschern durchaus vergleichbar sind (0,86 mmol Mo/ml Säulenvolumen). Als Säulendimensionen wurden daher für die Sorption von maximal 5 g MoO_3 und im Hinblick auf eine möglichst rasche Trennung 100 × 30 mm gewählt.

Elutionsverhalten von Alkali- und Erdalkalispuren bei der Molybdän-Matrixabtrennung auf Sephadex G-10

Untersuchungen über das Elutionsverhalten von Alkalispuren ergaben, daß bei geringer NH_4Cl-Konzentration der Aufgabelösung Kalium über den gesamten untersuchten Konzentrationsbereich mit gleichbleibend schlechter Ausbeute von etwa 50 % eluiert wird, während die Ausbeuten für Natrium erst ab etwa 300 ppm als quantitativ zu betrachten sind (Abb. 3). Immerhin ist bei Natrium eine Sorptionsisotherme erkennbar, während sich Kalium durchwegs statistisch auf stationäre innere

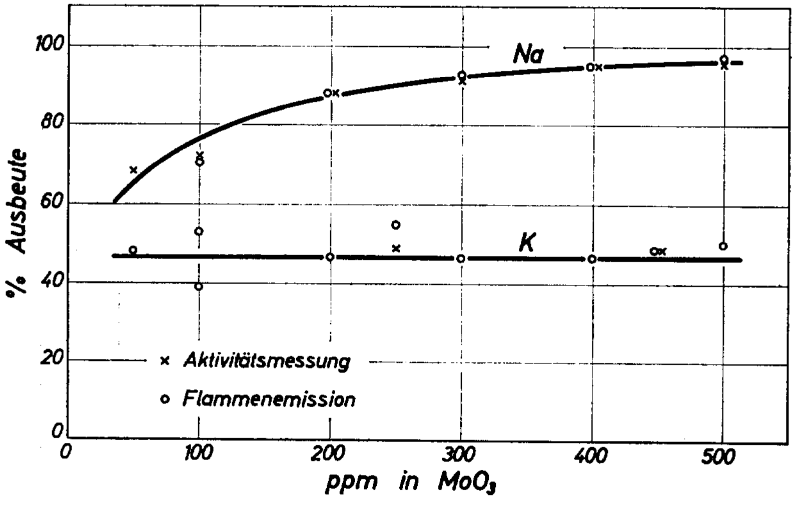


ABB. 3.—Alkalispurenverhalten bei der Mo-Matrixabtrennung bei niedriger NH_4Cl-Konzentration der Aufgabelösung.

Säulendimensionen: 120 × 30 mm; Zimmertemperatur; Tropfgeschwindigkeit: 100 ml/h. Aufgabelösung: jeweils 250 ml; 0,14*M* Mo (= 5 g MoO_3); pH-Wert 2,5; 0,05*M* NH_4Cl; Nachelution mit 100 ml 0,2*M* NH_4Cl. Gesamtelutionsvolumen 350 ml. Mo ist erst ab 350 ml im Eluat nachweisbar.

und mobile äußere Phase zu verteilen scheint. Ferner wurde das Elutionsverhalten von NaCl-Spuren auf reinen und mit Molybdän beladenen Sephadex G-10 Säulen untersucht: An reinen G-10 Säulen wurde NaCl mit einem Peakelutionsvolumen eluiert, das der Summe aus Zwischenkornvolumen und innerem Gelvolumen ($v_0 + v_i$) entspricht. An mit Molybdän beladenen Säulen erscheinen die ersten Natriumspuren beim *ca.* 2,5-fachen Peakelutionsvolumen des ersten Versuches. Die Ursache dieser Erscheinungen dürfte folgende sein.

Durch Bildung des Mo–NH_3-Glucosekomplexes wird die Sephadexsäule in eine Art "anorganischen Ionenaustauscher" verwandelt. Bekanntlich weist z.B. mikrokristallines Ammoniumphosphomolybdat hohe Selektivität für Kalium, Rubidium und Cäsium in sauren Lösungen auf.[7] Damit ist aber auch der Weg zur Überwindung dieser Schwierigkeit aufgezeigt: Bei Anwendung einer höheren NH_4Cl-Konzentration der Aufgabelösung verhindern die im riesigen Überschuß vorhandenen, praktisch gleich großen NH_4^+-Ionen die Kalium-Sorption und bedingen gleichzeitig eine bessere Komplexbildung des Molybdäns mit dem Sephadex.

Tabelle III gibt eine Übersicht über Ausbeuteuntersuchungen bei endgültig optimierten Bedingungen. Um Fehler durch Kontamination zu vermeiden und die Messungen mit konstanter hoher Präzision durchführen zu können, wurden radioaktiv markierte Lösungen und Gamma-Spektrometrie zur Endbestimmung herangezogen. Die Ausbeuten für Kobalt zeigen, daß die Methode auch zur Abtrennung anderer Metallspuren geeignet ist.

Tabelle III.—Ausbeuteuntersuchung bei endgültig optimierten Bedingungen

Element*	Aufgegeben, *ppm*	Ausbeute, %
$Na(+{}^{22}Na)$	trägerfrei	98, 99, 98
$K(+{}^{42}K)$	34	98,0
	50	96,0
	168	99,5
$Ca(+{}^{47}Ca)$	5	96,0
	7	98,0
$Co(+{}^{60}Co)$	100	97,0

* ${}^{22}Na$, ${}^{42}K$ und ${}^{47}Ca$ wurden in den Bereichen der Peaks bei 0,51, 1,52 bzw. 1,31 MeV gemessen.

Säulendimensionen: 100 × 30 mm; Zimmertemperatur; Tropfgeschwindigkeit: 100 ml/h.

Aufgabelösungen: jeweils 200 ml; 0,174*M* an Mo (= 5 g MoO_3); pH-Wert 2,5; *ca.* 2 g NH_4Cl/200 ml; Nachelution mit 100 ml 1*M* NH_4Cl (pH 2,5).

Zur spektroskopischen Endbestimmung

Die flammenphotometrische Alkali- und Erdalkalibestimmung erfolgte ohne Einengung des Säuleneluates nach Zugabe von 1000 ppm Cäsium als Strahlungspuffer. Interelementbeeinflussungen (besonders die des Natrium auf Kalium) werden dadurch hintangehalten. Eine Einengung der Säuleneluate zur Erhöhung der Nachweisempfindlichkeit ist zwar möglich, aber mühsam und bei Konzentrationen über 10 ppm unzweckmäßig (Die Vertreibung der Ammonsalze gelingt nach Einengung bis zur Krustenbildung durch portionsweise Zugabe (3–4 mal) von je 5 ml konz. HNO_3. Ein Verlust an Alkali- und Erdalkalispuren tritt dabei nicht auf).

Für die Erfassung von Natrium und Kalium wurde die Flammenemissionsspektralanalyse (Propan-Luft) verwendet, für Calcium und Magnesium die Atomabsorption (Preßluft-Acetylen).

Eichkurven

Molybdänprobelösungen wurden mit variierenden Mengen an Alkali- und Erdalkalispuren versetzt und zur Matrixabtrennung über die Säule geschickt. Für die Endauswertung wurden auf 2 verschiedenen Wegen Eichkurven erstellt:

(*a*) Die Eichlösungen enthielten neben dem zu bestimmenden Element 3% Ammoniumchlorid.

(*b*) Zur Erstellung von Eichlösungen wurde mit entsprechenden Zugaben an Alkali- und Erdalkalichloriden aufgestocktes Säuleneluat von reinem MoO_3 verwendet. Nach erfolgter Chromatographie wurden die Alkali- und Erdalkaligehalte der dotierten Proben gegen die aufgestockten Eluate als Eichlösungen vermessen und mit der tatsächlich zugesetzten Menge verglichen.

Im folgenden ist die Arbeitsvorschrift für MoO_3-Einwaagen von 2,5 g pro Säulentrennung wiedergegeben. Die Säulenkapazität reicht jedoch für Einwaagen bis zu 5,0 g MoO_3 (= 200 ml Aufgabelösung) pro Säulentrennung aus.

ARBEITSVORSCHRIFT

Probenvorbereitung

Molybdänmetallpulver oder -späne werden in möglichst wenig konzentrierter HNO_3 und konzentrierter HCl (1:1) gelöst (Teflonbecher) und zur Trockene eingedampft. Anschließend glüht man das entstehende MoO_3 drei Stunden bei 450° (Platinschale). MoO_2 wird mit konzentrierter HNO_3 durch leichtes Erhitzen in MoO_3 überführt und ebenfalls 3 Stunden bei 450° geglüht. Bei MoS_2 und Ammoniummolybdaten genügt dreistündiges Glühen bei 450°.

Es wird 6,25 g MoO_3 hierauf in einem Teflonbecher in *ca.* 50 ml H_2O suspendiert, auf 70–80° erwärmt und unter Rühren mit 8 ml Ammoniak (25 Gew.-%) versetzt. Die Auflösung erfolgt sofort. Dann wird auf *ca.* 200 ml verdünnt und 6 ml konzentrierte HCl (37 Gew.-%) zugegeben. Bei sehr unreinen Produkten bleibt vorhandenes SiO_2 ungelöst und muß abfiltriert werden. Die Lösung wird nun in einen Plastikmeßkolben überführt und auf 250 ml aufgefüllt; 2–3 ml werden zur pH-Messung entnommen. Der pH-Wert liegt meist bei 3,0–2,8. Nach Zugabe einiger Tropfen konz. HCl und Umschütteln wird der pH-Wert nochmals gemessen. Dies wird fortgesetzt, bis der pH-Wert von 2,5 erreicht ist. Auf diese Weise vermeidet man eine eventuelle Kaliumkontamination der Probelösung durch die Glaselektrode. Die angegebene Menge Ammoniak entspricht nach dem Ansäuern dem nötigen Ammoniumchloridüberschuß von *ca.* 1 g/100 ml Aufgabelösung. Dadurch wird die Zugabe von NH_4Cl überflüssig. Je 100 ml der so hergestellten Lösung (entsprechend einer Einwaage von je 2,5 g MoO_3) werden zu zwei parallelen Alkali- und Erdalkalibestimmungen verwendet. Nur frisch bereitete Lösungen führen unter strenger Einhaltung der angeführten Bedingungen zu reproduzierbaren Resultaten. Besonders bei Zimmertemperaturen unter 20° tritt bei längerem Stehen Ausfällung von Ammoniummolybdat ein.

Auch Ammoniummolybdate müssen vor der Auflösung mit Ammoniak in MoO_3 übergeführt werden, da sonst keine quantitative Sorption auf der Säule stattfindet. Vermutlich ergeben deren Lösungen bei der Ansäuerung andere, schlechter sorbierbare Aggregate als dies bei MoO_3 als Ausgangsmaterial der Fall ist.

Säulenchromatographie

Säulenbett: 100 × 30 mm Sephadex G-10 fine. Durchflußgeschwindigkeit: 0·14 ml/h.mm^2 (= 100 ml/h). Zimmertemperatur. Aufgabevolumen: 100 ml; Nachelution mit 100 ml 1*M* Ammoniumchlorid (pH 2,5).

Die ersten 30 ml Eluat werden verworfen, dann werden 150 ml Eluat in einem Plastikmeßzylinder gesammelt. Die Säulen werden durch Aufgabe von 200 ml 0,1*M* Ammonium-ÄDTE (pH 6, 100 ml/h), gefolgt von 150 ml 1*M* Ammoniumchlorid (pH 2,5) regeneriert. Die Säulen sind vor Licht durch Alu-Folie oder Kohlepapier zu schützen, da sonst intensive Blaufärbung des Säulenbettes eintritt und die Regenerierung erschwert ist. Eine leichte Blaufärbung des Säulenbettes ist unbedenklich. Die Säulen sind nach unserer Erfahrung praktisch unbegrenzt verwendbar.

Endbestimmung

Die flammenphotometrische Alkali- und Erdalkalianalyse erfolgt ohne Einengung im Eluat. Zu 150 ml Eluat wird jeweils 1 ml einer CsCl-Lösung zugesetzt, die 19 g CsCl/100 ml enthält. Dies entspricht einer Dotierung mit 1000 ppm Cs.

ANWENDUNG DER ENTWICKELTEN METHODE AUF KALIUM-ANALYSEN IN VERSCHIEDENEN MOLYBDÄNVERBINDUNGEN

Ein Beispiel der praktischen Anwendung der entwickelten Methode ist die Bestimmung des Kaliumgehaltes einer Reihe von MoO_3-, MoS_2- und Ammoniummolybdat-Rohstoffproben (Tab. IV). Zum Vergleich wurden einige Proben auch von einem Schiedslabor nach dort üblichen Methoden untersucht. Die Übereinstimmung kann, abgesehen von den Werten für MoS_2, als sehr gut bezeichnet werden. Ferner ist in Tab. V die Veränderung des Kaliumgehaltes in Molybdänvorprodukten und Sintermolybdän während des Erzeugungsganges zusammengestellt.

TABELLE IV.—KALIUM-ANALYSEN IN MOLYBDÄN-ROHSTOFFEN

Material	Eigene Ergebnisse (ppm)	Schiedslabor (ppm)
MoO_3 subl.	<20	<50
MoO_3 techn.	2250	2150
MoS_2-Konzentrat	65	255
Ammoniumdimolybdat	20	—
Ammoniumparamolybdat, (1)	135	—
Ammoniumparamolybdat, (2)	155	—

TABELLE V.—KALIUM-ANALYSEN IN MOLYBDÄNVORPRODUKTEN UND SINTERMOLYBDÄN

Material	Kaliumgehalt, *ppm* (Mittelwert aus 3 Parallelbestimmungen)
MoO_3, (1)	270
MoO_3, (2)	265
MoO_2, (1)	205
MoO_2, (2)	170
Mo-Pulver, (1)	60
Mo-Pulver, (2)	20
Mo-Stab, (1)	27
Mo-Stab, (2)	27

DISKUSSION

Zur Komplexbildung des Molybdäns mit Dextrangelen

Über die Komplexbildung des Molybdän(VI) mit aliphatischen Polyhydroxoverbindungen liegen zahlreiche Untersuchungen mit einander oft widersprechenden Ergebnissen vor.[8–14] So behaupten Bourne *et al.*,[10] daß nur diejenigen Monosaccharide mit Molybdän Komplexe bilden, welche ein *cis–cis* 1,2,3-triol System aufweisen.

Rimbach und Ley[11] finden jedoch Molybdän–Glucose Komplexe. Dieser Befund wird durch die vorliegende Untersuchung erhärtet. Das Gel mit der höchsten Gelkonzentration pro Volumeneinheit weist auch die höchste Sorptionskapazität für Molybdän auf. Im Sephadexgel LH-20 ist die Anzahl der 1,2,3-triolgruppen gegenüber den anderen eingesetzten Geltypen stark vermindert. Es tritt jedoch nur eine geringfügige Kapazitätsverminderung gegenüber G-15 ein, was auf den etwas geringeren Vernetzungsgrad von LH-20 zurückzuführen ist. Somit genügen zur Chelatkomplexbildung des Molydäns mit den Glucoseeinheiten der Dextrangele zwei benachbarte OH-Gruppen.

Übereinstimmend wird berichtet, daß die Molybdän-Polyhydroxoverbindungen nur in saurer Lösung stabil sind[12] (Optimum bei pH-Wert 2 und durch Alkalien zerstört werden. Eine Zunahme des pH-Wertes der Lösung bei Komplexbildung wurde beobachtet.[9,13] Dies wird nach dem von Püschel und Lassner[14] angegebenen Reaktionschema verständlich, das hier in etwas modifizierter Form wiedergegeben

$$[Mo(OH)_8]^{2-} + R(OH)_n \rightarrow [Mo(OH)_{8-x}R(OH)_n]^{-2+x} + xOH^-$$

wird. Der Übersichlichkeit halber wurde ein Molybdation zur Reaktion gebracht, obwohl es sich bei pH-Wert 2,5 und der relativ hohen Konzentration an Molybdän natürlich um Isopolysäuremoleküle handelt. Am Prinzip der Reaktion ändert diese Vereinfachung nichts. In Analogie zu Überlegungen betreffend die Chemie des Niobs und Tantals in wäßrigen Lösungen[15] wurde auch im vorliegenden Fall das Molybdation als vollkommen hydratisiert formuliert. Es ist anzunehmen, daß der Polymerisationsgrad des sorbierten Molybdäns nicht einheitlich ist.[16] Die Erniedrigung des Polymerisationsgrades bei sinkender Molybdän-Konzentration könnte zu schlechterer Sorbierbarkeit des Molybdäns bei niedriger Konzentration beitragen (vgl. Batch-Experimente). Daß jedoch die Löslichkeit des Mo–NH_3–Glucosekomplexes eine wohl dominierende Rolle spielt, geht daraus hervor, daß die Molybdän-Durchbruchskapazität auf Sephadex G-10 Säulen sehr abhängig von der NH_4^+-Konzentration der Probe und auch der Nachelutionslösung ist. Schon Frey[17] und Soubarew-Chatelain[18] isolierten salzartige Molybdän–Zuckerkomplexe, die NH_3 komplex im Anion gebunden hatten. Die hier vorgeschlagene Konstitutionsformel führt zu Mo–NH_3–Glucosekomplexen chelatartigen Charakters, was die Bildung des Molybdäns an die Glucoseeinheiten des Gels sowie die Bindung der einzelnen Molybdänatome untereinander betrifft. Die entstehenden Komplexe sind ungeladen. Die offensichtlich hohe Affinität dieser Komplexe für K^+ und NH_4^+ dürfte in Analogie zu Salzen verschiedener Heteropolysäuren des Molybdäns und Wolframs[7] auf sterische Effekte zurückzuführen sein, wie sie auch für die Austauscheigenschaften der Zeolithe bekannt sind. Die stabilere Komplexbildung bei Anwesenheit von NH_4Cl dürfte

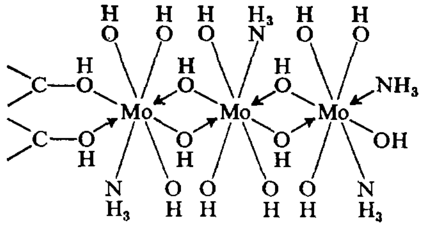


Abb. 4.—Vereinfachtes Reaktionsschema von Molybdän mit aliphatischen Polyhydroxoverbindungen—Mögliche Konstitutionsformel des Mo-NH_3-Glucosekomplexes.

durch eine Erniedrigung der Gitterenergie des entstehenden Komplexes bei Einbau von NH_3-Gruppen verusacht sein. Die Komplexbildung deutet sich durch leichte Gelbfärbung des Säulenbettes in der Sorptionszone an. Bei Lichteinwirkung verfärbt sich das Säulenbett blau, offenbar durch Bildung von Mischoxidhydraten infolge schwacher Reduktion durch die UV-Strahlung.

Zur flammenphotometrischen Alkali- und Erdalkalibestimmung

Direktzerstäuberbrenner vom Ringspalttyp (Zeiss-Flammenansatz FA1, Beckman DU) sind wegen der relativ hohen Ammoniumchloridkonzentration in den Säuleneluaten nicht anwendbar. Es tritt sehr bald Verstopfung der Ansaugkanüle ein. Die Hohlkathodenlampen des zur Verfügung stehenden Zeiß-Atomabsorptionszusatzes FA2 waren bei keinem Lampenstrom auf annähernd konstante Strahlungsintensität zu bringen. Die Bestimmung von Natrium und Kalium in Emission auf dem Eppendorf-Gerät sowie die Erfassung von Calcium und Magnesium in Absorption mit den Geräten Perkin–Elmer 290B und Jarrel Ash Atomsorb verliefen komplikationslos.

Wie bei allen Verfahren der direkten flammenphotometrischen Erfassung von Metallspuren ist auch hier ein Verdünnungsfaktor gegeben, d.h. die ursprünglich in 2,5 g Einwaage vorhandenen Spuren werden nach erfolgter Matrixabtrennung in einem Volumen von 150 ml erfaßt (Faktor 60). Bei niedrigen Spurengehalten arbeitet man somit (vor allem bei Calcium) an der Grenze der exakt quantitativen Erfaßbarkeit.

Durch den Ammoniumchloridgehalt von etwa 3% in den Säuleneluaten tritt insbesondere bei Flammenemission eine beträchtliche Depression der Strahlungsintensität gegenüber rein wäßrigen Lösungen ein.

Die genaue Überprüfung des Analysenverfahrens erfolgte unter Anwendung von aufgestockten Säuleneluaten als Eichlösung. Reine Molybdänlösungen wurden vor Aufgabe auf die Säule mit bekannten Mengen an Natrium, Kalium, Calcium und Magnesium versetzt, chromatographiert und die Alkali- und Erdalkaligehalte gegen die aufgestockten Eluate (als Eichlösungen) vermessen. Die Übereinstimmung mit der tatsächlich zugesetzten Menge war zufriedenstellend. Dieses Verfahren erfaßt sämtliche Analysenparameter. Die so erhaltenen Werte stimmten jedoch auch mit Resultaten überein, die man erhält, wenn dieselben Eluate mit entsprechend dotierten Ammoniumchloridlösungen als Eichlösungen verglichen wurden. Auch die nach beiden Verfahren ermittelten Blindwerte für das eingesetzte reine MoO_3 waren praktisch identisch. Die Reproduzierbarkeit ist für beide Methoden gleich. Bis etwa 60 ppm liegt der Variationskoeffizient bei ±10%, darüber bei ±5%. Zur Aufstellung der Eichkurven kann daher eine 3%ige Ammoniumchloridlösung verwendet werden, die mit Salzsäure auf pH 2,5 gebracht wurde.

Summary—A new column chromatographic method for the separation of molybdenum as matrix element from traces of alkali and alkaline earth metals is introduced. The molybdenum(VI) sorption is achieved on Sephadex G-10 columns at pH 2·5 in ammonium chloride solutions, by the formation of an Mo–NH_3–glucose complex. Alkali and alkaline earth metal traces remain quantitatively in the effluent and are determined by flame-emission and atomic-absorption spectrophotometry respectively. Separation time is slightly less than 2 hr. With some automation the procedure is well suited for routine trace analysis of sodium, potassium, calcium and magnesium in metallic molybdenum, MoO_3, MoO_2, MoS_2, *etc.* The coefficient of variation is ±10% up to 60 ppm, and ±5% at above 60 ppm.

Résumé—On présente une nouvelle méthode de chromatographie sur colonne pour la séparation du molybdène en tant qu'élément de matrice de traces de métaux alcalins et alcalino-terreux. La sorption du molybdène(VI) est réalisée sur des colonnes de Sephadex G-10 à pH 2,5 dans des solutions de chlorure d'ammonium, par la formation d'un complexe Mo-NH_3-glucose. Les traces de métaux alcalins et alcalino-terreux restent quantitativement dans l'effluent et sont dosées par spectrophotométrie d'émission de flamme et spectrophotométrie d'absorption atomique respectivement. Le temps de séparation est légèrement inférieur à 2 h. Avec une certaine automatisation, la technique convient bien à l'analyse de routine de traces de sodium, potassium, calcium et magnésium dans le molybdène métallique, MoO_3, MoO_2, MoS_2, etc. Le coefficient de variation est de ±10% jusqu'à 60 ppm, et de ±5% au-delà de 60 ppm.

LITERATUR

1. A. J. Hegedüs, J. Neugebauer und M. Dvorszky, *Mikrochim. Acta*, 1959, 282.
2. H. G. Döge, *Anal. Chim. Acta*, 1967, **38**, 207.
3. E. F. Spano und T. E. Green, *Anal. Chem.*, 1966, **38**, 1341.
4. H. J. Eckstein, ed., *Spurenanalyse in hochschmelzenden Metallen*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1970.
5. P. Onitter, A. Simanits und A. Elek, *Talanta*, 1967, **14**, 417.
6. F. Feigl, *Qualitative Analysis by Spot Tests*, Elsevier, Amsterdam, 1946.
7. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
8. D. Gernez, *Compt. Rend.*, 1891, **112**, 1360.
9. E. Richardson, *J. Inorg. Nucl. Chem.*, 1959, **9**, 273.
10. E. J. Bourne, D. H. Hutson und H. Weigel, *J. Chem. Soc.*, 1960, 4252.
11. E. Rimbach und P. Ley, *Z. Physik. Chem.*, 1922, **100**, 393.
12. E. J. Bourne, D. H. Hutson und H. Weigel, *J. Chem. Soc.*, 1961, 35.
13. P. Souchay, *Bull. Soc. Chim. France*, 1949, 122.
14. R. Püschel und E. Lassner, *Chelates and Chelating agents in the Analytical Chemistry of Molybdenum and Tungsten* in H. A. Flaschka und A. J. Barnard Jr., eds., Dekker, New York, 1967.
15. E. Lassner und R. Püschel, *J. Less-Common Metals*, 1967, **12**, 146.
16. P. Souchay, *Ions minéraux condensés*, Masson, Paris, 1969.
17. H. Frey, *Ann. Chim. (Paris)*, 1943, **18**, 5.
18. Z. Soubarew-Chatelain, *Compt. Rend.*, 1939, **208**, 1652.

Talanta, 1972, Vol. 19, pp. 915 to 925. Pergamon Press. Printed in Northern Ireland

COMPUTER CALCULATION OF ACTIVATION ENERGIES OF IRREVERSIBLE ELECTRODE PROCESSES AT A DROPPING MERCURY ELECTRODE

D. R. CROW and S. L. LING
Thames Polytechnic, London S.E.18, U.K.

(*Received* 26 *August* 1971. *Accepted* 29 *November* 1971)

Summary—A computer program has been written for calculation of the activation energies of irreversible electrode processes at a dropping mercury electrode, based on the variation of current and half-wave potential with temperature. The program calculates the half-wave potential, the transfer coefficient, and the activation energies of the diffusion process and the irreversible electrode process. It has been written in both ALGOL and FORTRAN.

POLAROGRAPHIC methods for obtaining thermodynamic parameters relating to coordination compounds have already been established. Knowledge of the activation energy and the frequency factor for a reduction process can be of importance to inorganic chemists. These two parameters can yield important information regarding the mechanism of the electrode reaction. The first is a measure of structural changes within the depolarizer during the acceptance of electrons, and the second indicates the orientation of the depolarizer at the electrode surface.

Experimentally, the absolute value of the activation energy cannot be determined; it is possible, however, to determine a relative value. Values of the activation energy have usually been determined from the temperature-dependence of current–voltage curves without concentration polarization. A simple polarographic method based on that proposed by Vlček,[1] provides two means for determining activation energy. The first requires measurement of the change in current, $i_{\text{irrev.}}$, with temperature, from which the activation energy is determined from the dependence of log $i_{\text{irrev.}}/(i_d - i_{\text{irrev.}})$ on $1/T$ where i_d is the diffusion current. The second depends on the measurement of the change of half-wave potential with temperature. Both approaches involve a large number of experimental results and graphical plots, especially logarithmic plots. Therefore, extremely laborious and time-consuming numerical computation, although simple, is necessary. It is therefore not surprising that not very many values of such parameters have been obtained this way. In this field one may take advantage of the capacity of high-speed digital computers.

A computer program has been published for analysis of polarograms,[2] which does not include activation energy calculations. We have here a general ALGOL program—POLENACT—for calculating the half-wave potential ($E_{1/2}$), transfer coefficient (α), the activation energy of the diffusion process (Q_D) and the activation energy of the irreversible electrode process (Q), using the two approaches outlined above. We publish this program in the hope that it may be of some help to others.

METHOD

For an irreversible diffusion-controlled system, the half-wave potential and the transfer coefficient can be determined from the so-called logarithmic analysis of the current–voltage curve. The equation of the irreversible polarographic curve for a cathodic reduction may be expressed as

$$E = E_{1/2} - \frac{2{\cdot}303RT}{\alpha nF}\log\frac{i}{i_d - i} \tag{1}$$

where n is the number of electrons exchanged in the electrode reaction, ($R = 8{\cdot}314$ V.C.K^{-1}, $F = 96486{\cdot}82$ C), T is the temperature in K and i denotes the current in μA at a given potential E. It follows from equation (1) that a plot of $\log i/(i_d - i)$ *vs.* E is a straight line with intercept $E_{1/2}$ and a slope from which α is directly determinable.

The two equations proposed by Vlček for computing the activation energy of the electrode processes are based on the equation for an irreversible polarographic wave and also on the assumption that the rate-constant of the electrode process satisfies the Arrhenius equations. The first of the two equations is expressed as

$$\log\frac{i}{i_d - i} = \log A' - \frac{Q - Q_D/2}{2{\cdot}303RT} \tag{2}$$

where A' is the "apparent frequency factor."

By means of equation (2), the value of $(Q - Q_D/2)$ can be directly evaluated graphically from the dependence of $\log i/(i_d - i)$ on $1/T$.

Alternatively, we can determine an arbitrary activation energy Q', referred to some arbitrary constant potential E'. Here, the observation of the change of half-wave potential with the temperature gives the corresponding form of equation (2) as

$$\frac{\alpha nF(E_{1/2} - E')}{2{\cdot}303RT} = \log A - \frac{Q' - Q_D/2}{2{\cdot}303RT} \tag{3}$$

Once again, the value of $(Q' - Q_D/2)$ can be evaluated graphically from the plot of $\alpha nF(E_{1/2} - E')/2{\cdot}303RT$ *vs.* $1/T$.

However, in calculating the value of Q (or Q'), the value of Q_D must be known independently. This value can be determined from the dependence of the diffusion current on temperature, the slope of the $\log i_d$ *vs.* $1/T$ plots being $\frac{1}{2}(Q_D/2{\cdot}303R)$.[3]

Using the program described in the Appendix, the computer reads in from the cards the arbitrary potential at which the activation energy is to be determined, the number of temperature sets of polarograms, the relevant potentials, the temperature, the diffusion current and the relevant current-values for each polarogram of the system. Applying equation (1), the computer then calculates, using the least-squares method,[4] the half-wave potentials, the transfer coefficient, and the slope and intercept of the $\log i/(i_d - i)$ *vs.* $1/T$ plot, for each polarogram of a system at different temperatures. With the results obtained above, the machine proceeds to compute the activation energy of diffusion, and then follows with activation energies of the electrode process, from equations (2) and (3). The results are finally printed out in tabular form.

DISCUSSION

The program has been tested for the hexa-aquonickel(II) ion. The solution was $5 \times 10^{-4}M$ nickel in $0{\cdot}1M$ potassium nitrate plus 0·0004% of Triton-X. The temperature range used was from 20° to 50° and the reference electrode was a saturated

```
                         GENERAL LISTING (XRLP) 09/11/71

DOC SOURCE-PROG
'TRACE' 2
'BEGIN''INTEGER'X,SET,SYS,J,N,R,Y,P,TOTAL,CHECK;
'REAL'E2;
'PROCEDURE'LINE(B,D,F,G,NL,XL,INTERCEPTS,SLOPES,R);
'VALUE'NL,XL;
'REAL'B,D,F,G,INTERCEPTS,SLOPES;
'INTEGER'R,NL,XL;
'COMMENT' THIS PROCEDURE IS FOR WORKING OUT THE BEST STRAIGHT LINE
            THROUGH A SERIES OF POINTS;
'BEGIN''REAL'BB,DD,FF,GG,HH;
'INTEGER'CC;
BB:=DD:=FF:=GG:=0;
'FOR'R:=NL'STEP'1'UNTIL'XL'DO''BEGIN'
BB:=BB+B;
DD:=DD+D;
FF:=FF+F;
GG:=GG+G;
'END';
CC:=XL-NL+1;
HH:=CC*GG-DD↑2;
INTERCEPTS:=(BB*GG-FF*DD)/HH;
SLOPES:=(CC*FF-BB*DD)/HH;
'END'LINE;
SELECT INPUT(1);
SELECT OUTPUT(2);
CHECK:=READ;
'COMMENT' IF CHECK IS ONE THEN ONLY THE LOG VALUES, E1/2, AND ALPHA
    WILL BE WORKED OUT. OTHER NUMBERS WILL WORK OUT THE COMPLETE
    PROGRAMME. SYS IS NO. OF POLAROGRAPHIC SYSTEM AND SET IS THE NO.
    OF POLAROGRAMS IN THE SYSTEM AND TOTAL IS THE TOTAL NO. OF
    POTENTIAL VALUES REQUIRED (WITHIN THE LINEAR RANGE) FOR
    CALCULATING THE WHOLE SYSTEM, N I'S NO. OF ELECTRONS INVOLVED IN
    THE TRANSFER PROCESS, E2 IS THE REF. POTENTIAL USED FOR
    EXTRAPOLATION AND ALSO USED IN THE E1/2 METHOD;
SYS:=READ;
Y:=1;
'IF'CHECK=1'THEN'
WRITETEXT('(''('P20S')'ANALYSIS%OF%POLAROGRAMS')')
'ELSE'
WRITETEXT('(''('P20S')'ANALYSIS%OF%POLAROGRAMS%AND%CALCULATION%
OF%ACTIVATION%ENERGIES')');
SETNO:NEWLINE(10);
SPACE(10);
COPYTEXT('('SYSTEM')');
E2:=READ;
SET:=READ;
TOTAL:=READ;
N:=READ;
R:=1;
X:=TOTAL;
'BEGIN''REAL''ARRAY'ID,T,LOGID,ALPHA,E1,ECAL,ENH,ALPE,ALPENH[1:SET],
I,LOG[1:SET,R:X],E[1:X];
'COMMENT' READ IN ALL POTENTIAL NEEDED FOR THE SYSTEM;
'FOR'J:=1'STEP'1'UNTIL'X'DO''BEGIN'
E[J]:=READ;
'FOR'P:=1'STEP'1'UNTIL'SET'DO'
```

```
I[P,J]:=0;
'END';
P:=1;
'COMMFNT' STAPT OF LOG ANALYSIS;
LOOP:T[P]:=READ;
ECAL[P]:=0.4526-0.0007*T[P];
ID[P]:=READ;
'COMMFNT'READ IN UPPER AND LOWER BOUNDS OF CURRENT;
R:=READ;
X:=READ;
'FOR'J:=R'STEP'1'UNTIL'X'DO''BFGIN'
I[P,J]:=READ;
LOG[P,J]:=0.434294*LN(I[P,J]/(ID[P]-I[P,J]));
'END';
'BEGIN''REAL'INT,SLOPE,B,D,F,G,H;
'INTEGER'C;
'COMMENT' WORKING OUT THE PARAMETERS OF THE POLAROGRAM;
B:=D:=F:=G:=0;
'FOR'J:=R'STEP'1'UNTIL'X'DO''BFGIN'
B:=B+LOG[P,J];
D:=D+E[J];
F:=F+E[J]*LOG[P,J];
G:=G+E[J]↑2;
'END';
C:=X-R+1;
H:=C*G-D↑2;
INT:=(B*G-F*D)/H;
SLOPE:=(C*F-B*D)/H;
E1[P]:=INT/(-SLOPE);
ALPHA[P]:=SLOPE*T[P]*0.0001985/N;
WRITETEXT('(''('6C')'HALF%WAVE%POTENTIAL%AND%ELECTRON%
TRANSFER%COEFFICIFNT%(ALPHA)%ONLY'('2C')'ALL%POTENTIAL%
VALUES%ARE%MEASURED%IN%VOLTS%AGAINST%SCE%AND%CURRENTS%
ARE%IN%MICROAMPS.'('3C')'TEMPERATURE')');
PRINT(T[P],6,1);
WRITETEXT('('K'('2C')'ID')');
PRINT(ID[P],6,3);
WRITETEXT('('MICROAMPS'('2C')'E'('9S')'I'('7S')'
LOG'('75')'ERRORS')');
'FOR'J:=R'STEP'1'UNTIL'X'DO''BEGIN'NEWLINE(1);
PRINT(E[J],1,3);
PRINT(I[P,J],2,3);
PRINT(LOG[P,J],1,4);
PRINT(LOG[P,J]-(INT+SLOPE*E[J]),1,3);
'END';
WRITETEXT('(''('ZC')'INTERCFPT')');
PRINT(INT,6,5);
WRITETEXT('(''('8S')'SLOPE')');
PRINT(SLOPF,7,3);
WRITFTEXT('(''('2C')'HALF%WAVE%POTENTIAL')');
PRINT(E1[P],5,3);
WRITETEXT('('VOLTS%VS.%SCE'('2C')'ALPHA')');
PRINT(ALPHA[P],4,3);
'END';
P:=P+1;
'IF'P'LE'SET'THEN''GOTO'LOOP'ELSE'
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'
ENH[P]:=E1[P]-ECAL[P];
'COMMENT' ENH IS E1/2 AT NHE, ALPHE IS ALPHA*E1/2(SCE), AND
```

```
              ALPENH IS ALPHA*E1/2(NHE);
ALPE[P]:=E1[P]*ALPHA[P];
ALPENH[P]:=ENH[P]*ALPHA[P];
'END';
WRITETEXT('(''('6C')'TABULATION%OF%TEMPERATURE,%ID,%E1/2,%
ALPHA,%E1/2*ALPHA.'('6C')'T(K)'('6S')'ID'('5S')'E1/2(SCE)'('3S')'
E1/2(NHE)'('3S')'ALPHA'('5S')'ALP*E1/2(NHE)'('3S')'ALP*E1/2(SCE)')');
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'NEWLINE(1);
PRINT(T[P],3,1);
PRINT(ID[P],2,3);
PRINT(E1[P],1,4);
PRINT(ENH[P],4,4);
PRINT(ALPHA[P],3,4);
PRINT(ALPENH[P],3,4);
PRINT(ALPE[P],9,4);
'END';
J:=1;
WRITETEXT('(''('6C')'TABULATION%OF%DATA%AT%CONSTANT%POTENTIAL%
FROM%ABOVE%DATA')');
TABULATION:WRITETEXT('(''('3C')'E')');
PRINT(E[J],1,3);
WRITETEXT('('VOLTS%VS.%SCE'('2C')'T(K)'('6S')'
I(MICROAMPS)'('6S')'LOG(I/ID-I)')');
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'NEWLINE(1);
PRINT(T[P],4,1);
'IF'I[P,J]'NE'0'THEN''BEGIN'
PRINT(I[P,J],2,3);
PRINT(LOG[P,J],9,4);
'END''ELSE'
'END';
J:=J+1;
'IF'J'LE'TOTAL'THEN''GOTO'TABULATION 'ELSE'
'IF'CHECK=1'THEN''GOTO'TERMINATE'ELSE'
'BEGIN''REAL''ARRAY'E12,AET,S[1:SET],QEQ,Q[1:TOTAL];
'REAL'QE,QD,REFQ,ARBQ,ARBQCA;
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'
LOGID[P]:=0.434294*LN(ID[P]);
S[P]:=1/T[P];
'END';
'BEGIN''REAL'INTT,SLOP;
'COMMENT' WORKING OUT THE DIFFUSION ENERGY;
LINF(LOGID[R],S[R],S[R]*LOGID[R],S[R]↑2,1,SET,INTT,SLOP,R);
QE:=9.152*(-SLOP);
QD:=QE*4.184/1000;
WRITETEXT('(''('6C')'ACTIVATION%ENERGY%OF%THE%DIFFUSION%PROCESS
'('4S')'QD'('3C1S')'ID'('6S')'LOGID'('6S')'T'('6S')'1/T'('8S')'
ERRORS')');
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'NEWLINE(1);
PRINT(ID[P],1,3);
PRINT(LOGID[P],1,4);
PRINT(T[P],3,1);
PRINT(S[P],1,7);
PRINT(LOGID[P]-(INTT+SLOP*S[P]),1,3);
'END';
WRITETEXT('(''('2C')'INTERCEPT')');
PRINT(INTT,4,5);
WRITETEXT('(''('8S')'SLOPE')');
PRINT(SLOP,7,3);
WRITETEXT('(''('2C')'QD')');
```

```
PRINT(QD,6,1);
WRITETEXT('('KJ      ')');
PRINT(QE,5,1);
WRITETEXT('('CALORIES')');
'END';
'BEGIN''REAL'BQ,DQ,FQ,GQ,HQ,INTER,GRAD;
'INTEGER'CQ;
'COMMENT' WORK OUT ACTIVATION ENERGIES ONLY WHEN FOUR OR MORE
          LOG VALUES ARE AVAILABLE;
J:=1;
REPEAT:P:=1;
BQ:=CQ:=DQ:=FQ:=GQ:=0;
SORT:'IF'I[P,J]=0'THEN''GOTO'NEXT'ELSE'
BQ:=BQ+LOG[P,J];
CQ:=CQ+1;
DQ:=DQ+S[P];
FQ:=FQ+S[P]*LOG[P,J];
GQ:=GQ+S[P]↑2;
NEXT:P:=P+1;
'IF'P'LE'SET'THEN''GOTO'SORT'ELSE'
'IF'CQ'GE'4'THEN''BEGIN'
HQ:=CQ*GQ-DQ↑2;
INTER:=(BQ*GQ-FQ*DQ)/HQ;
GRAD:=(CQ*FQ-BQ*DQ)/HQ;
QEQ[J]:=QE*0.5+4.576*(-GRAD);
Q[J]:=QEQ[J]*4.184/1000;
WRITETEXT('(''('6C')'ACTIVATION%ENERGY%OF%IRREVERSIBLE%ELECTRODE%
PROCESS'('4S')'Q'('2C')'METHOD%USED:%LOG%CURRENT%ANALYSIS%AND%
TEMPERATURE'('4C')'E')');
PRINT(E[J],4,2);
WRITETEXT('('VOLTS%VS.%SCE'('2C')'QD')');
PRINT(QD,6,2);
WRITETEXT('('KJ      '('2C')'LOG'('9S')'T'('6S')'1/T'('9S')'
ERRORS')');
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'NEWLINE(1);
'IF'I[P,J]'NE'0'THEN''BEGIN'
PRINT(LOG[P,J],1,4);
PRINT(T[P],3,1);
PRINT(S[P],1,7);
PRINT(LOG[P,J]-(INTER+GRAD*S[P]),1,3);
'END'
'ELSE''END';
WRITETEXT('(''('2C')'INTERCEPT')');
PRINT(INTER,4,5);
WRITETEXT('(''('8S')'SLOPE')');
PRINT(GRAD,7,3);
WRITETEXT('(''('2C')'Q')');
PRINT(Q[J],6,2);
WRITETEXT('('KJ/MOLE')');
PRINT(QEQ[J],6,1);
WRITETEXT('('CALORIES')');
'END''ELSE'
Q[J]:=QEQ[J]:=0;
J:=J+1;
'IF'J'LE'TOTAL'THEN''GOTO'REPEAT'ELSE'
WRITETEXT('(''('6C')'TABLE%OF%ACTIVATION%ENERGIES%FOR%VARIOUS%
POTENTIALS%FROM%ABOVE%SETS%OF%CALCULATION'('3C')'QD')');
PRINT(QD,6,2);
WRITETEXT('('KJ      '('2C')'E(VOLTS)'('3S')'
```

```
Q(KJ/MOLE)'('3S')'Q(KCAL/MOLE)')');
'FOR'J:=1'STEP'1'UNTIL'TOTAL'DO''BEGIN'
'IF'Q[J]'NE'0'THEN''BEGIN'
NEWLINE(1);
PRINT(E[J],2,3);
PRINT(Q[J],4,2);
PRINT(QEQ[J]/1000,6,4);
'END'
'ELSE''END';
'COMMENT' WORK OUT ACTIVATION ENERGY FROM E1/2 AND ALPHA VALUES
          AND USING A REFERENCE POTENTIAL;
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'
E12[P]:=E1[P]-E2;
AET[P]:=(ALPHA[P]*N*96486.82*E12[P]*S[P])/19.147142;
'END';
'BEGIN''REAL'CUT,INCLINE;
LINE(AET[R],S[R],AET[R]*S[R],S[R]↑2,1,SET,CUT,INCLINE,R);
ARBQCA:=QE*0.5+4.576*INCLINE;
ARBQ:=ARBQCA*4.184/1000;
WRITETEXT('(''('6C')'ACTIVATION%ENEGY%OF%IRREVERSIBLE%ELECTRODE%
PROCESS'('4S')'Q'('2C')'METHOD%USED:%REFERRED%TO%AN%ARBITARY%
CONSTANT%POTENTIAL%AND%HALF%WAVE%POTENTIAL.'('2C')'ARBITARY%
POTENTIAL')');
PRINT(E2,5,2);
WRITETEXT('('VOLTS%VS.%SCE'('2C9S')'F(E,T,N)=ALPHA*N*F(E1/2-E[ARBITARY]
)/2.303RT'('2C')'QD')');
PRINT(QD,6,2);
WRITETEXT('('KJ      '('2C')'E1/2'('6S')'ALPHA'('6S')'
F(E,T,N)'('4S')'T'('11S')'1/T'('7S')'ERRORS')');
'FOR'P:=1'STEP'1'UNTIL'SET'DO''BEGIN'NEWLINE(1);
PRINT(E1[P],1,4);
PRINT(ALPHA[P],1,4);
PRINT(AFT[P],3,3);
PRINT(T[P],5,1);
PRINT(S[P],2,7);
PRINT(AET[P]-(CUT+INCLINE*S[P]),5,3);
'END';
WRITETEXT('(''('2C')'INTERCEPT')');
PRINT(CUT,3,3);
WRITETEXT('(''('8S')'SLOPE')');
PRINT(INCLINE,7,3);
WRITETEXT('(''('2C')'Q')');
PRINT(ARBQ,6,1);
WRITETEXT('('KJ/MOLE')');
PRINT(ARBQCA,6,1);
WRITETEXT('('CALORIES')');
'END';
'BEGIN''REAL'INTCEPT,GRADT,BA,DA,FA,GA,HA;
'INTEGER'CA;
'COMMENT' EXTRAPOLATING THE VALUE OF Q TO THE REFERENCE POTENTIAL
          FROM THE LOG CURRENT METHOD;
J:=1;
BA:=CA:=DA:=FA:=GA:=0;
EXTRAP:'IF'Q[J]=0'THEN''GOTO'EXT'ELSE'
BA:=BA+Q[J];
CA:=CA+1;
DA:=DA+E[J];
FA:=FA+E[J]*Q[J];
GA:=GA+E[J]↑2;
EXT:J:=J+1;
'IF'J'LE'TOTAL'THEN''GOTO'EXTRAP'ELSE'
HA:=CA*GA-DA↑2;
INTCEPT:=(BA*GA-FA*DA)/HA;
GRADT:=(CA*FA-BA*DA)/HA;
REFQ:=INTCEPT+GRADT*E2;
WRITETEXT('(''('6C')'PARAMETERS%OBTAINED%FROM%EXTRAPOLATING%
THE%Q%VALUES%USING%LOG%ANALYSIS'('4C')'SLOPE%OBTAINED%IS')');
PRINT(GRADT,7,3);
WRITETEXT('('KJ/VOLT'('2C')'ARBITARY%POTENTIAL')');
PRINT(E2,5,2);
WRITETEXT('('VOLTS%VS.%SCE'('2C')'ACTIVATION%ENERGY%
AT%ABOVE%POTENTIAL:')');
PRINT(REFQ,6,2);
WRITETEXT('('KJ/MOLE'('2C')'ACTIVATION%ENERGY%BY%ALPHA%
AND%E1/2%METHOD%AT%THE%SAME%REFERENCE%POTENTIAL:')');
PRINT(ARBQ,6,2);
WRITETEXT('('KJ/MOLE')');
'END''END'
'END';
TERMINATE:Y:=Y+1;
'IF'Y'LE'SYS'THEN''GOTO'SETNO'ELSE'
'END'
'END';
```

TABLE I.—EXPERIMENTAL RESULTS FROM POLAROGRAMS

	E	*i*, *μA*						
No.	(*V vs.* SCE)	293·3 K	298·0 K	303·0 K	308·0 K	313·0 K	318·0 K	323·0 K
1	0·87	—	—	—	—	—	—	2·120
2	0·88	—	—	—	—	—	—	2·440
3	0·89	—	—	—	—	—	1·730	2·800
4	0·90	—	—	—	—	—	2·070	3·190
5	0·91	—	—	—	—	1·530	2·410	3·570
6	0·92	—	—	—	—	1·820	2·810	3·950
7	0·93	—	—	—	1·320	2·190	3·190	4·330
8	0·94	—	—	—	1·680	2·590	3·580	4·720
9	0·95	—	—	1·340	2·030	2·980	3·960	5·110
10	0·96	—	—	1·685	2·420	3·370	4·360	5·400
11	0·97	—	1·370	2·030	2·860	3·780	4·720	—
12	0·98	—	1·670	2·425	3·300	4·220	5·060	—
13	0·99	1·370	2·050	2·870	3·720	4·590	5·350	—
14	1·00	1·715	2·490	3·300	4·170	4·930	—	—
15	1·01	2·110	2·920	3·730	4·510	5·200	—	—
16	1·02	2·555	3·335	4·130	4·880	—	—	—
17	1·03	3·000	3·830	4·500	—	—	—	—
18	1·04	3·430	4·165	4·810	—	—	—	—
19	1·05	3·820	4·510	—	—	—	—	—
20	1·06	4·205	4·785	—	—	—	—	—
21	1·07	4·500	—	—	—	—	—	—
Diffusion current, i_d		5·450	5·800	6·080	6·150	6·470	6·720	7·020

TABLE II.—VALUES OF HALF-WAVE POTENTIALS AND TRANSFER COEFFICIENTS AT DIFFERENT TEMPERATURES

T, K	i_d, *μA*	$E_{1/2}$(SCE) *V*	$E_{1/2}$(NHE) *V*	α	$\alpha E_{1/2}$(NHE)	$\alpha E_{1/2}$(SCE)
293·3	5·450	1·0236	0·7763	0·4182	0·3247	0·4281
298·0	5·800	1·0093	0·7653	0·3927	0·3006	0·3964
303·0	6·080	0·9939	0·7534	0·3760	0·2832	0·3737
308·0	6·150	0·9746	0·7376	0·3850	0·2840	0·3752
313·0	6·470	0·9559	0·7224	0·3504	0·2531	0·3349
318·0	6·720	0·9341	0·7041	0·3299	0·2323	0·3082
323·0	7·020	0·9079	0·6814	0·3165	0·2157	0·2874

TABLE III.—ACTIVATION ENERGIES OF THE ELECTRODE PROCESS AT VARIOUS POTENTIALS, FROM THE CURRENT METHOD

Activation energy of diffusion process, Q_D = 12·6 kJ/mole (3·02 kcal/mole)		
E, *V vs.* SCE	*Q*, *kJ/mole*	*Q*, *kcal/mole*
0·93	103·7	24·80
0·94	99·4	23·76
0·95	96·8	23·14
0·96	93·7	22·39
0·97	86·6	20·70
0·98	86·4	20·64
0·99	83·6	19·99
1·00	82·2	19·65
1·01	79·5	19·00
1·02	80·7	19·28

TABLE IV.—ACTIVATION ENERGIES OBTAINED FROM THE TWO EQUATIONS REFERRED TO AN ARBITRARY POTENTIAL

Arbitrary potential	0.5 V vs SCE
Activation energy obtained from equation (2) extrapolated to above potential	218.96 kJ/mole
Activation energy obtained from equation (3)	214.44 kJ/mole

calomel electrode (SCE). An ICL 1902A digital computer took 54 sec to calculate all the required parameters for the system. Table I gives the data obtained from the experimental polarograms. The computer-calculated parameters are given in Tables II, III and IV.

Zusammenfassung—Zur Berechnung der Aktivierungsenergien irreversibler Elektrodenprozesse an einer Quecksilbertropfelektrode wurde ein Computerprogramm geschrieben, das auf der Temperaturabhängigkeit des Stroms und des Halbwellenpotentials beruht. Das Programm berechnet das Halbwellenpotential, den Durchtrittsfaktor und die Aktivierungsenergien des Diffusionsvorgangs sowie des irreversiblen Elektrodenprozesses. Es ist in ALGOL und FORTRAN geschrieben.

Résumé—On a écrit un programme pour calculatrice pour le calcul des énergies d'activation de processus d'électrode irréversibles à l'électrode à goutte de mercure, basé sur la variation du courant et du potentiel de demi-vague avec la température. Le programme calcule le potentiel de demi-vague, le coefficient de transfert et les énergies d'activation du processus de diffusion et du processus d'électrode irréversible. Il a été écrit en ALGOL et FORTRAN.

REFERENCES

1. A. A. Vlček, *Collection Czech. Chem. Commun.* 1959, **24**, 3538.
2. S. Savage and W. D. Shults, *Nucl. Sci. Abstr.*, 1965, **19**, 5800.
3. L. Gierst, *Thesis*, University of Brussels, 1958.
4. P. R. Bevington, *Data Reduction and Error Analysis for Physical Sciences*, p. 92, McGraw-Hill, New York, 1969.

APPENDIX

The computer program POLENACT in ALGOL 60 is divided into two sections. The first section is used to read the data from the cards and perform the logarithmic analysis on the polarograms. It

TABLE V.—EXPLANATION OF SYMBOLS IN POLENACT

real

E2 = arbitrary potential; int = intercept of log $i/(i_d - i)$ *vs.* E plot; slope = slope of that plot; b, d, f, g, h, bq, dq, fq, gq, hq, ba, da, fa, ga, ha = numerical values in general; qe = diffusion activation energy in calories; qd = diffusion activation energy in kJ/mole; arbq = activation energy of electrode process at an arbitrary potential in kJ/mole; arbqca = as arbq but in cal/mole; refq = activation energy of electrode process extrapolated to the arbitrary potential from Q *vs.* E plot; intt and slop = intercept and slope of log i_d *vs.* $1/T$ plot respectively; inter and grad = intercept and slope of log $i/(i_d - i)$ *vs.* $1/T$ plot respectively; cut and incline = intercept and slope of $\alpha nF(E - E')/2{\cdot}303\,RT$ *vs.* $1/T$ plot respectively; intcept and gradt = intercept and slope of Q *vs.* E plot respectively.

integer (nr. = number)

set = nr. of sets of polarograms in the system; sys = nr. of systems; c, ca, cq, y, j, p = integers in general; n = nr. of electrons involved in the transfer process; r = upper bound nr. of the potential for the polarogram; x = lower bound nr. of the potential for the polarogram; total = total nr. of potential used; check = the section of program to be run.

real array

p can have values from 1 to set; j can have values from 1 to total; id[p] = diffusion current of the polarogram at t[p]; t[p] = temperature at which polarogram is measured; logid[p] = $\log_{10}$ id[p]; alpha[p] = transfer coefficient of the polarogram at t[p]; E1[p] = half-wave potential of the polarogram at t[p]; ecal[p] = potential of SCE at temperature t[p]; enh[p] = E1[p] − ecal[p]; alpe[p] = product of alpha[p] and E1[p]; alpenh[p] = product of enh[p] and alpha[p]; i[p, j] = current measured at t[p] and E[j]; log [p, j] = $\log_{10}$(i[p, j]/id[p] − i[p, j]); E[j] = potential applied; E12[p] = E1[p] − E1 at t[p]; AET[p] = (alpha[p] × n × F × E12[p])/2·303R × t[p]; s[p] = 1/t[p]; QEQ[j] = activation energy at E[j] in cal/mole; Q[j] = as QEQ[j] but in kJ/mole.

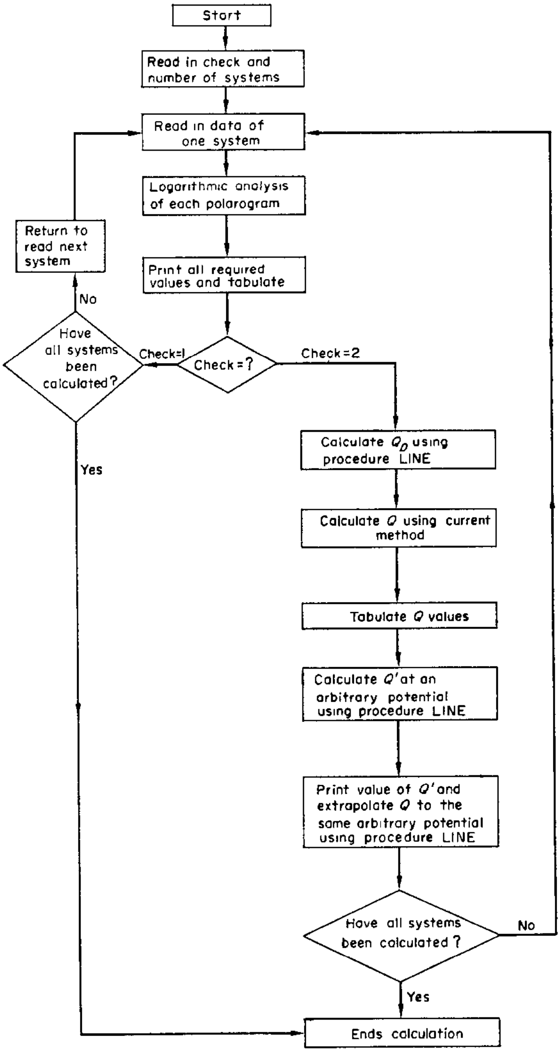


FIG. 1.—Flow-chart for computer program POLENACT.

TABLE VI.—INPUT DATA

1. Section of POLENACT to be run (either 1 or 2; see flow-chart).
2. Number of system to be run.
3. Title of the system to be run. (SYSTEM is the copy-text procedure).
4. Arbitrary potential.
5. Number of polarograms in the system.
6. Total number of potential used in the system (see Table I).
7. Number of electrons involved in the transfer process.
8. Complete series of the potential values used in the system.
9. Temperature of the polarogram.
10. Diffusion current for that temperature.
11. Upper bound number of the potential value (see Table I).
12. Lower bound number of the potential value (see Table I).
13. Current values for the above temperature.

Note: 1 and 2 are used only once, at the beginning of the input; 3–8 are used only once for each system and 9–13 are repeated for the whole of the system to be worked out. Example (only part of data input extracted from Table I).

```
2, 1,
HEXA-AQUONICKEL ION, 0·1M KNO3 SYSTEM
0·5, 7, 21, 2,
0·87, 0·88, 0·89, 0·90, 0·91, 0·92, 0·93, 0·94, 0·95, 0·96, 0·97,
0·98, 0·99, 1·00, 1·01, 1·02, 1·03, 1·04, 1·05, 1·06, 1·07,
293·3, 5·45, 13, 21,
1·370, 1·715, 2·110, 2·550, 3·00, 3·430, 3·820, 4·205, 4·500,
298·0, 5·80, 11, 20,
1·370, 1·6970, 2·050, 2·490, 2·920, 3·335, 3·830, 4·165, 4·510, 4·785,
```

This is repeated until all seven sets are completed as shown in Table I.

will then summarize the parameters of the polarograms—the half-wave potentials (first referred to SCE and, after making the necessary temperature correction, the normal hydrogen electrode, NHE). At the same time the values of $\alpha E_{1/2}$ will also be computed. Finally, it rearranges all the log $i/(i_d - i)$ values and temperatures at constant potential.

The second half of POLENACT calculates the activation energy of diffusion, in calories or kilojoules per mole. Having done this, it then works out the activation energy of the electrode process from the current at different applied potentials (when four or more sets of data are available). Then it will tabulate Q values at different potentials. Using the $E_{1/2}$ shifts and α, it proceeds to calculate the value of Q' at the required arbitrary potential. Finally, the values of Q are extrapolated to this arbitrary potential for comparison purpose.

Table V explains the symbols used. A simplified flow-chart showing the calculation is shown in Fig. 1. The procedure called LINE has been used to calculate the best fit for the straight line, by the least-squares method. The program translated into FORTRAN will be supplied on request. Since FORTRAN is much closer to the machine code, computing time is reduced. With the translated program, the time taken to do the same calculations was 40 sec. The input data for POLENACT are shown in Table VI.

Talanta, 1972, Vol. 19, pp. 927 to 936. Pergamon Press. Printed in Northern Ireland

SOME OPTICAL STUDIES WITH THE AIR-ACETYLENE FLAME

K. M. ALDOUS*, R. F. BROWNER†, D. CLARK, R. M. DAGNALL
and T. S. WEST
Chemistry Department, Imperial College, London S.W.7 2AY, U.K.

(*Received* 25 *October* 1971. *Accepted* 2 *December* 1971)

Summary—The application of Schlieren and shadow techniques for the study of flame processes is discussed in relation to analytically useful premixed flames. The information obtained, particularly with shadowgraphs, may be correlated with the measured signals and signal noise in atomic-absorption and flame-emission spectrometry.

OPTICAL methods employing Schlieren and shadowgraph techniques have been used extensively in combustion research for examining refractive-index fields,[1] particularly when information on such fundamental parameters as burning velocities or energy-release profiles has been required. However, there appears to have been no attempt to correlate the photographic records obtained by these methods with quantitative observations on the behaviour of metal atoms when nebulized into flames.

It is known that turbulent *diffusion* flames, such as those produced with Beckman burners, have a higher emissive background than the corresponding laminar flames[2] and it has also been observed that atomic species introduced into them are subject to more severe interelement interference[3] than in laminar flames. Though, as an adjunct to these observations, it is generally agreed that turbulence in *pre-mixed* flames is also undesirable, and various workers have published Schlieren[3,4,5] and shadow[6] records of several flames, the studies were purely qualitative and no conclusions were drawn indicating just how turbulence in pre-mixed flames influences analytical measurements.

The purposes of this study were therefore to examine Schlieren and shadow techniques as a means of observing flame processes (particularly the effect of flame separation) in some analytically useful flames, and to correlate this information with signals obtained from atomic-absorption and flame-emission measurements. In this context, changes in signal magnitude and signal noise are of particular interest as they are likely to be influenced directly by the flame processes.

The work described in this communication indicates that net changes in free atom fractions due to variations in the temperature or chemical composition of the flame gases can be a direct consequence of flame turbulence in premixed flames, as can the signal noise due to fluctuations of the atomic concentration in the flame.

INFORMATION PROVIDED BY OPTICAL TECHNIQUES

General theory

The theory and applications of Schlieren, shadow and interferometric techniques have been reviewed most thoroughly by Weinberg[1] and here we summarize only the salient features which are of direct relevance to the present study. The optical

---

* Present address: Division of Laboratories and Research, N.Y. State Health Department, Albany, N.Y. 12201, U.S.A.

† Present address: Department of Chemistry, University of Florida, Gainesville 32601, U.S.A.

methods mentioned provide means of measuring refractive index gradients in gases by photographic techniques and hence of defining regions over which the processes which produce such changes are occurring.

In the shadow method, light from a point source of illumination is passed through the test zone onto a screen. Any optical disturbance which takes place within the zone and which produces a refractive index gradient normal to the direction of the light-beam results in a local change of illumination on the screen. Refractive index gradients parallel to the light-beam cause no change in screen illumination.

In Schlieren photography, a parallel beam of light, after passing through the test zone, is brought to a focus at a "marking aperture" (which may take the form of a knife-edge, a pin-hole or a neutral optical wedge) by another lens. The aperture removes from the image (which in the absence of the marking aperture would be a normal image of the flame) the rays undeflected by the flame, whilst allowing some of the deflected rays to pass. An optical arrangement which may be used for shadow work and converted for use in Schlieren photography by the incorporation of only one further component (the marking aperture) is shown in Figs. 1 and 2. With these arrangements, the positioning of the flame with respect to the lens (*F*) is varied, depending on whether shadowgraph or Schlieren records are required.

Both optical methods provide the following information. They indicate the positions and dimensions of the primary and secondary reaction zones, as these are regions over which rapid refractive index changes are occurring. By the shapes of the zones they indicate the contours of the refractive index gradients in the burning or burned gases. A wrinkled appearance of a zone shows turbulence. They indicate the rate of refractive index change by the sharpness and degree of darkening of the zone (*e.g.*, primary reaction zones of laminar flames give much sharper images than do the zones of secondary diffusion flames).

Time variable processes

The optical observation of rapid fluctuations in the flame is important even though the higher frequency fluctuations may not register as noise on the recorder read-out (owing to its limited frequency bandpass) when the radiative emission from the flame is observed. Nevertheless, these fluctuations will give rise to overall changes in the

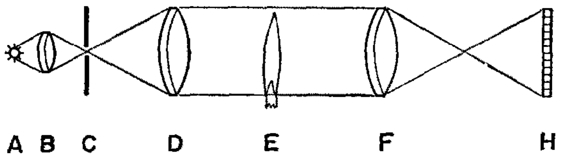


FIG. 1.—Shadow optics. *A*—Real source. *B*—Condenser lens. *C*—Aperture (effective source). *D*—Collimating lens. *E*—Test zone. *F*—Magnifying lens. *H*—Film.

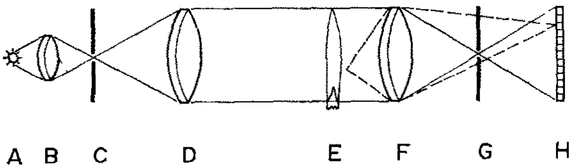


FIG. 2.—Schlieren optics. Optical components: *A*, *B*, *C*, *E*, *H*—as in Fig. 1. *D*—Schlieren lens. *F*—Projection lens. *G*—"Marking aperture".

composition of the burned gases, because of the different combustion processes induced. Changes in gas composition, which will also be associated with changes in gas temperature, may alter the free atom fraction and the magnitude of thermal emission signals from solutions nebulized into the flame.

Influence of measurement time on photographic record

All turbulent phenomena exhibit fluctuating refractive index fields. In this study exposure times of 1·5 msec were found effectively to "freeze" the turbulent phenomena occurring within the flames examined.

Signal measurements

In atomic-absorption spectrometry, when all the obvious variables which effect the total concentration of the element (free and combined) in the flame (such as nebulization rate, flame path-length, *etc*) are fixed, then the signal is a direct comparative measure of the free atom fraction, β. In flame-emission spectrometry, the signal magnitude is again dependent on β, but is also further influenced by the flame temperature, because of the nature of the radiative process.

Noise measurements

The noise in any measured signal, whether from atomic absorption or flame emission, is a combination of many components. Those noise components which are unrelated to flame processes are of no relevance to this work and can be eliminated from measurements of the total signal noise by the subtraction of quadratic components.

For a spectrometric system with a fixed electronic (noise) bandpass (Δf), the total root mean square noise voltage, N_T, may be related to the independent root mean square noise components, N_i, by the relationship:[7]

$$N_T = [\sum(N_i)^2]^{1/2} \tag{1}$$

This summation includes all the independent root mean square noise components which contribute to N_T.* In this particular instance only one noise component is of interest, the noise (from atoms in the flame) induced by flame processes, and this may be represented as N_F. As a direct corollary of the signal magnitude in atomic absorption and atomic emission, the signal noise, N_F, will measure fluctuations in the free atom concentration, β. In atomic emission it will also measure fluctuations in the flame temperature. Experimentally, N_T is measured as the total root mean square noise in the analytical signal and N_F is obtained by subtracting from this the remaining noise components as measured by the root mean square noise of the baseline, thus:

$$N_F = [N_T^2 - (N_i - N_F)^2]^{1/2} \tag{2}$$

This eliminates from the noise the components which are a consequence of electronic circuitry, stray room-light or hollow-cathode lamp instability in atomic-absorption measurements. As only noise which originates in the flame itself can be related to

* Winefordner *et al.* have used relationships of this kind in order to determine the magnitude of noise signals in atomic-emission,[8,9] atomic-absorption[10,9] and atomic-fluorescence spectrometry.[11] Reference should be made to these publications for a more detailed discussion of all the factors which may give rise to noise in atomic flame spectrometry.

optical observations of the flame gases, in all subsequent discussion this noise alone will be considered and will be referred to as "signal noise".

The apparent frequency of this noise as it registers on a recorder will be limited by the effective bandpass of the whole read-out system. However, the root mean square value of this waveform is a valid and convenient *comparative* measure of noise resulting from fluctuating processes in the flame.

For the purpose of this discussion, it is convenient to consider signal noise as originating from two separate sources. First there is nebulization noise. This noise should remain a constant proportion of the signal magnitude and is not amenable to measurement by Schlieren or shadow records of the flame gases although the spray supply itself can be studied by these means. Secondly there are fluctuations in the burned gases themselves. In a stable laminar flame this will be reduced to a minimum and will be of much smaller magnitude than in a turbulent flame. However stable and laminar a flame may appear to be, there will exist within it local variations in temperature and gas composition which will produce noise both in the background emission from the flame (flame flicker noise) and in any signal which is dependent on atomic concentrations in the flame. When the signal noise is *not* a constant proportion of the signal magnitude, even though the same solution is being nebulized, then it may be assumed that the deviation from proportionality is a measure of the flame fluctuations.

EXPERIMENTAL

Optics

There are numerous possible experimental arrangements for Schlieren and shadow photography. The optical systems employed in this work were shown in Figs. 1 and 2. Lenses were used throughout.

In the shadow system the flame position (*E*) is not critical, provided that it is not optically conjugate with the film plane, *i.e.*, a focused image of (*E*) is not formed at (*H*) by the lens (*F*).

For Schlieren photography, the flame *must* be optically conjugate with the film plane. In addition, a pinhole matched to (*C*) is placed at (*G*) and this acts as the marking aperture. Exposure times of 1/1000 sec nominal (1·5 msec actual, electronically measured) were used for all the photographic records and this effectively "froze" most flame fluctuations. Photographs were taken on Ilford F.P.4 120 Professional Roll Film.

Flames

Circular flames of *ca.* 10 mm diameter provided adequate photographic contrast and were also easier to align than long-path flames. Nevertheless conclusions drawn from their behaviour can be related to the behaviour of such flames. The influence of shielding gases on the stability of long-path flames should be more pronounced than with the cylindrical flame, as the area of contact and mixing of gases will occupy a greater proportion of the whole flame. However, the reduction in the background emission signal will be less, as the outer mantle corresponds to a smaller proportion of the total optical path through such a flame. The flames were produced on both capillary burners[13] and burners of the Méker type (manufactured by Beckman Research and Industrial Instrument Corporation Limited, Worsley Bridge Road, London S.E.26). Both types of burner had provision for gas sheathing.

Records were obtained for both air–acetylene and nitrous oxide–acetylene flames on burners of this type, with varying degrees of nitrogen separation. However, the information provided by the nitrous oxide–acetylene flame was no different in nature from that obtained with the air–acetylene flame. For all further work, including atomic-absorption and flame-emission signal measurements, the air–acetylene flame alone was used.

RESULTS

Comparison of results obtained by shadow and Schlieren photography

All optical records of flame disturbances were made alternately with both the shadow and Schlieren methods. As shadowgrams were especially sensitive to rapid changes in the refractive index field normal to the optical path, gradual changes across the flame ends do not register strongly and a flat, seemingly two-dimensional, picture is obtained (Plates 1–4 and 6–8). The Schlieren records have a three-dimensional appearance (Plate 5), which is a result of the greater responsiveness of the technique to the small components of refractive index change, normal to the light path, which occur at the flame ends.

The one instance where Schlieren photography has a clear advantage in the quality of the record produced is when flames of very high emissive background (such as nitrous oxide–acetylene) are to be studied. Here the marking aperture considerably reduces the light intensity from the flame, which would in its absence (as in shadow work) pass directly to the film and reduce the image contrast.

In view of the simplicity of the shadow method it is to be recommended for visual studies of laminar flames of low emissive background, and only shadowgrams will be discussed further.

Information obtained from shadowgrams of air–acetylene flames

General. The unseparated fuel-rich air–acetylene flame maintained on a capillary burner is exceptionally stable and laminar (Plate 1)*, up to the height of *ca* 57 mm. The leaner flame (not shown) is more nearly cylindrical in shape, with less expansion at all levels.

The same fuel-rich flame on a Beckman RIIC burner (Plate 6) has a larger initial diameter, showing greater expansion at the flame base, but reaches approximately the same diameter as the flame maintained on the capillary burner, at 30 mm above the primary zones. The initial expansion of gases, being more rapid, is less laminar. The more diffuse secondary reaction zone also indicates that the secondary combustion process is less sharply defined. The unevenness of the top of the flame illustrates what may also be visually observed, that this flame is more susceptible to draughts.

Flame background. Progressive separation of the air–acetylene flame on the capillary burner with an outer sheath of nitrogen, produces changes both in flame shape and laminarity. Plates 2, 3 and 4 show the effects of nitrogen flow-rates of 2, 6 and 10 l./min. From these representative photographs (selected from a set covering also all intermediate flows), the best compromise between efficient separation and induced turbulence, at a height of measurement 15 mm above the primary cones, would seem to occur at 6 l./min. Reference to Fig. 3(*i*) shows that the most efficient removal of OH emission does indeed occur at 6 l./min nitrogen flow.

At a position of measurement 30 mm above the primary reaction zones, separation with flow-rates above 6 l./min might be expected to lead to increased turbulence. Figure 3(*i*)(*c*) does show a slight increase in signal at flow-rates above 6 l./min, indicating that the induced turbulence is producing some air entrainment. This leads to increased combustion, with a consequent increase in OH emission.

From the noise curves (Fig. 3(*ii*)), the signal:noise ratio at 15 mm height in the flame passes through a minimum at a nitrogen flow of 6 l./min. In other words, a nitrogen flow of 6 l./min stabilizes the hot flame gases by diminishing their fluctuations.

---

* This may be contrasted with results of Rann[4] whose air–acetylene flame maintained on a Méker type burner showed extreme turbulence right from the base of the flame. This could only be reduced by flame shielding. The unshielded capillary burner flame appears as laminar as Rann's shielded flame. This shows how an unsatisfactory burner design may produce unstable flames.

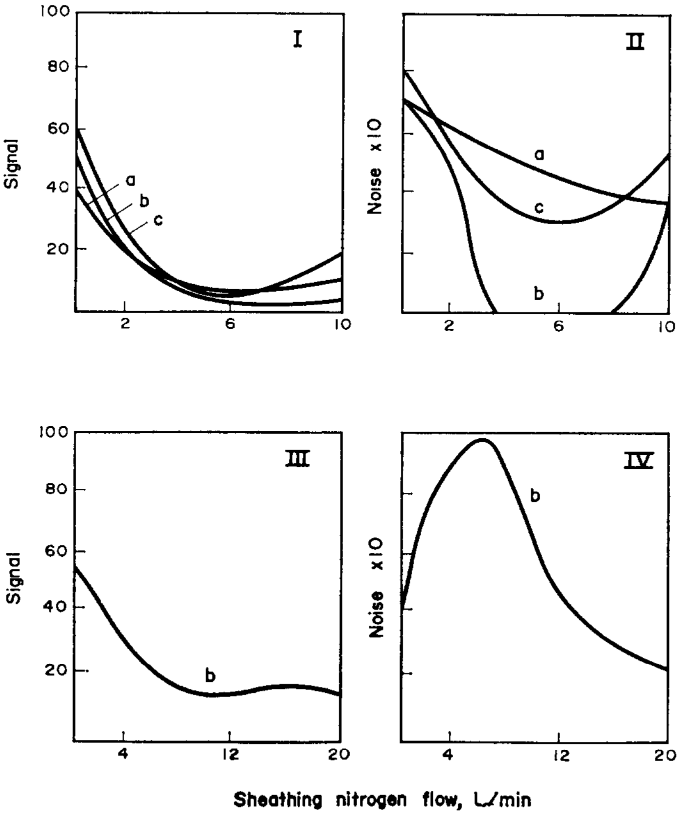
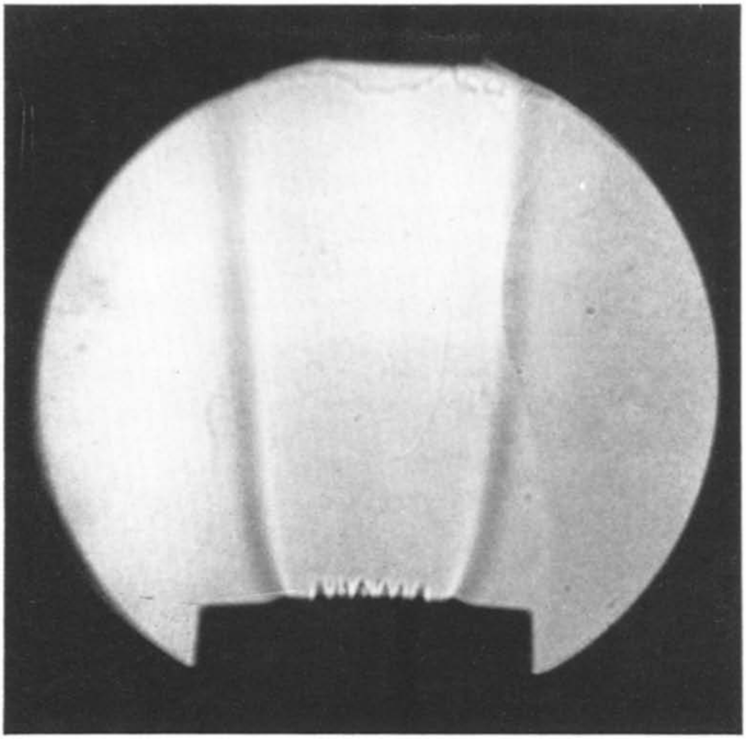


Fig. 3.—Emission and noise from fuel-rich air-C_2H_2 flames. (*i*) OH emission with capillary burner, (*ii*) OH emission noise with capillary burner, (*iii*) OH emission with Beckmann RIIC burner, (*iv*) OH emission noise with Beckmann RIIC burner. Height of observation above primary reaction zones: *a*—3 mm; *b*—15 mm; *c*—30 mm.

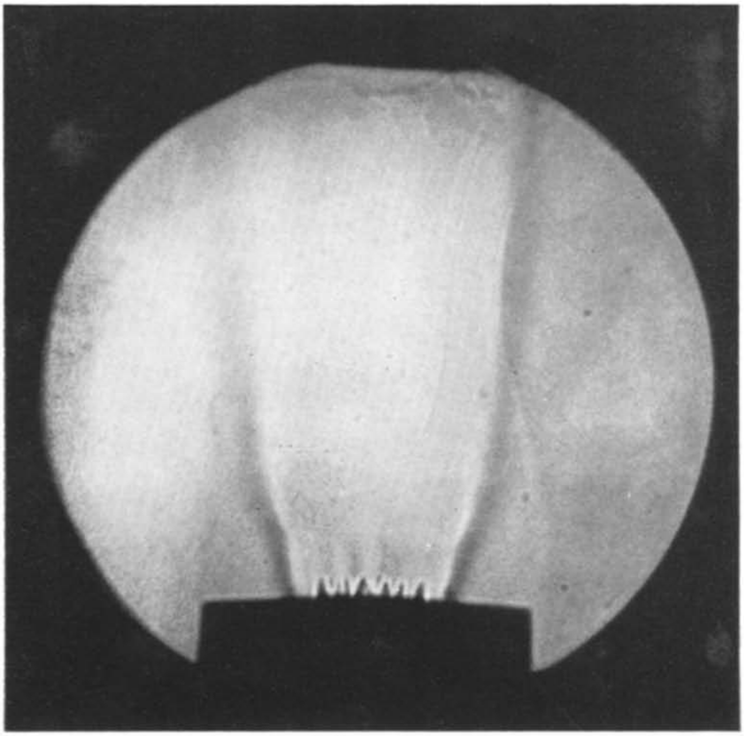
However, this increase in stability of the flame zones is not clearly seen on the shadowgrams because the *un*separated flame is so stable and only regions of greater turbulence than this show clearly on the photographs. Increasing the flow-rate to 10 l./min causes optical inhomogeneities in the gases, appearing as increased noise, and these are compatible with an examination of the flow patterns as shown by the shadowgrams.

The noise curves also show that noise levels measured high in the flame (*c*) are greater than those measured in the central regions (*b*) *at all nitrogen flow-rates*. This again accords with the photographs (Plates 2–4). Here the higher regions of the flame are seen to be more turbulent than the central regions at all separation flows.

The information provided by the shadowgrams can also be correlated with the variation of OH emission signals with height (Fig. 4). With no shielding [Fig. 4(*i*)(*a*) and 4(*ii*)(*a*)] the signal:noise ratio is approximately constant with height. The shadowgram (Plate 1) also shows no visible variation of optical inhomogeneities or turbulence with height. With a 6 l./min flow of shielding gas the signal:noise ratio passes through a pronounced minimum at a measurement height of 15 mm. The relevant shadowgram (Plate 3) shows some inhomogeneity low in the flame, where the gases are close to the primary zones, and also slight turbulence in the outer flame



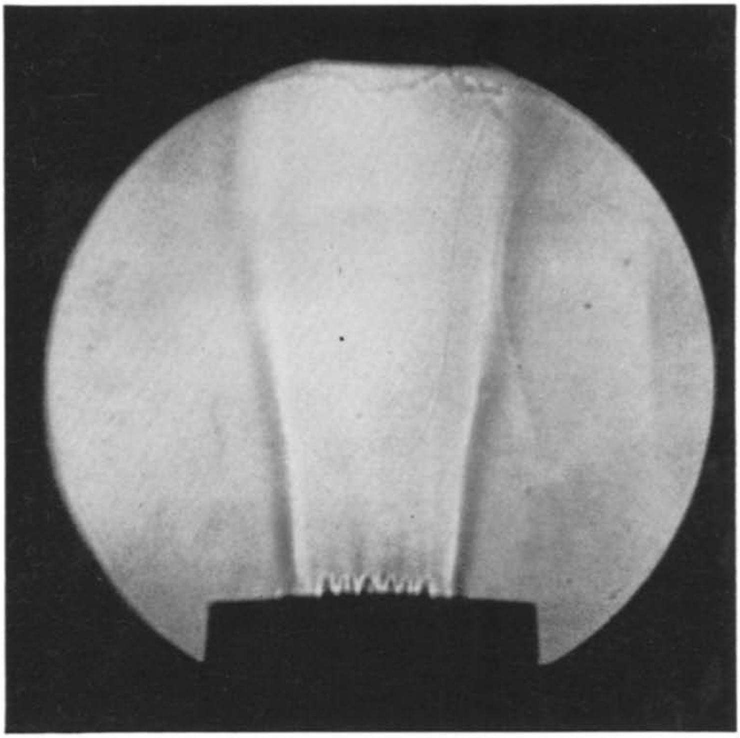
1



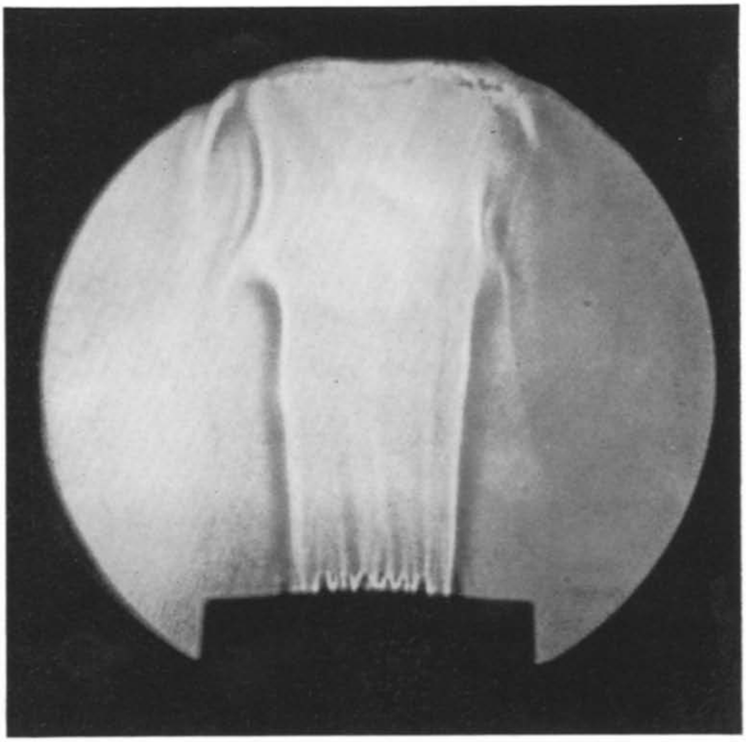
2

Plates 1–2.—*Shadowgrams of fuel-rich air–acetylene flames on capillary burner.*

1. Normal flame.
2. 2 l./min flow of nitrogen (for separation of flame).



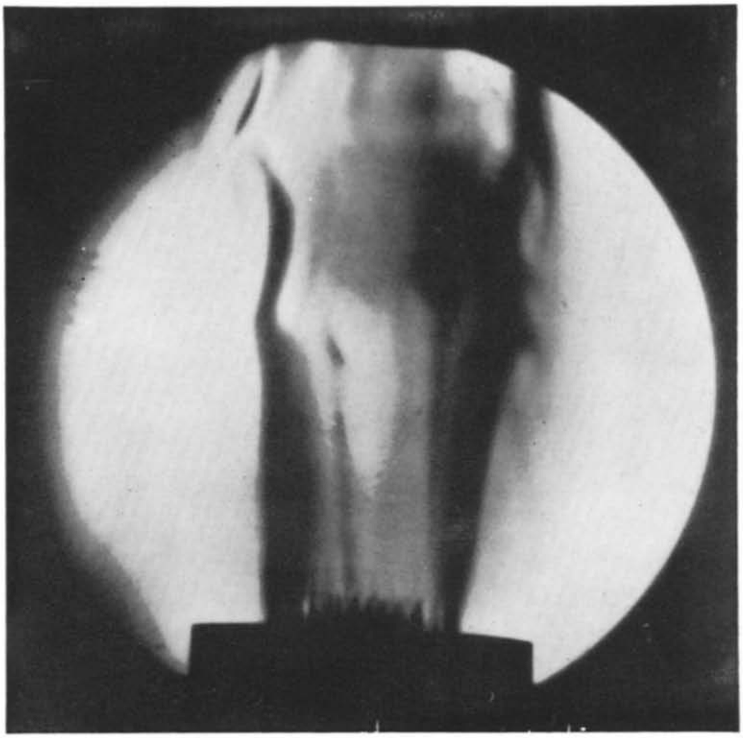
3



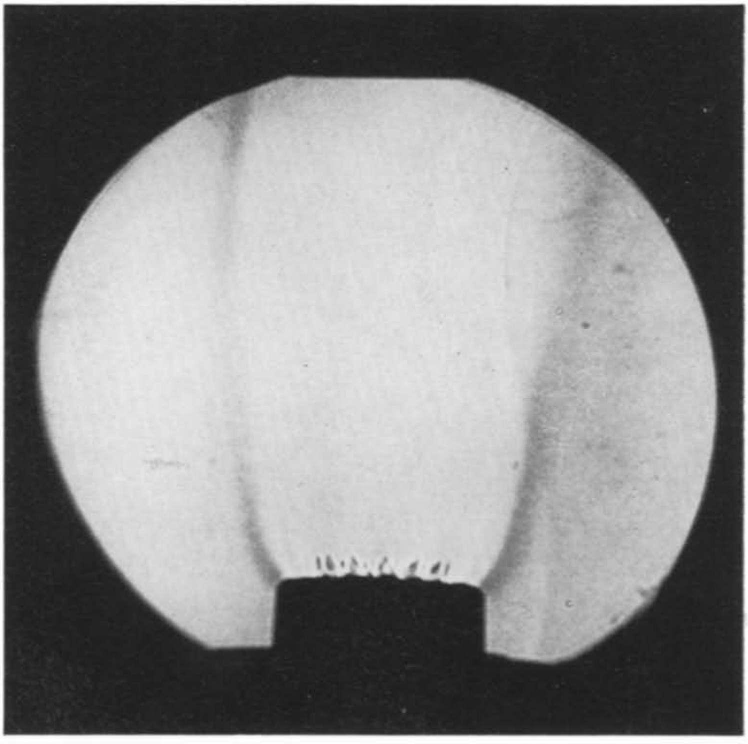
4

Plates 3–4.—*Shadowgrams of fuel-rich air–acetylene flames on capillary burner.*

3. 6 l./min of nitrogen.
4. 10 l./min of nitrogen.



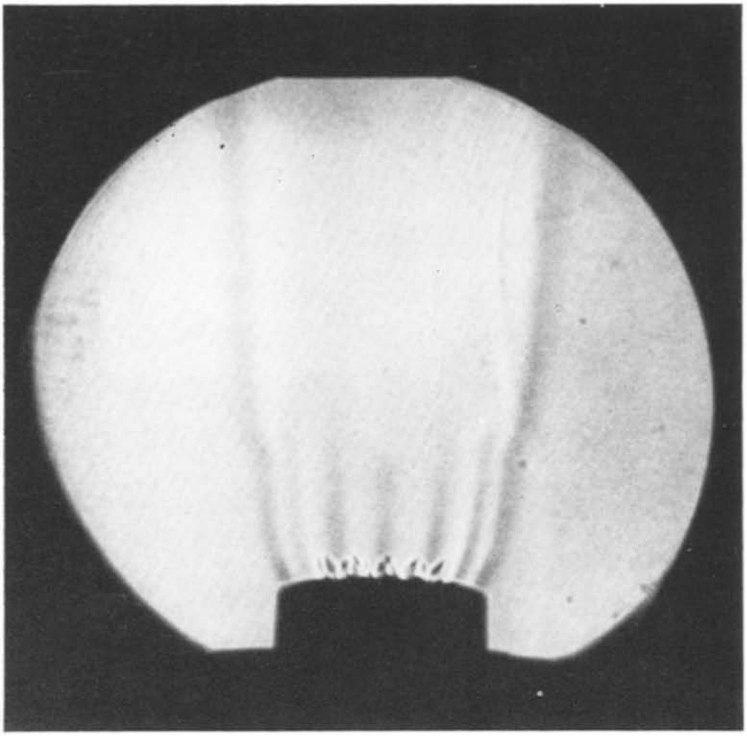
5



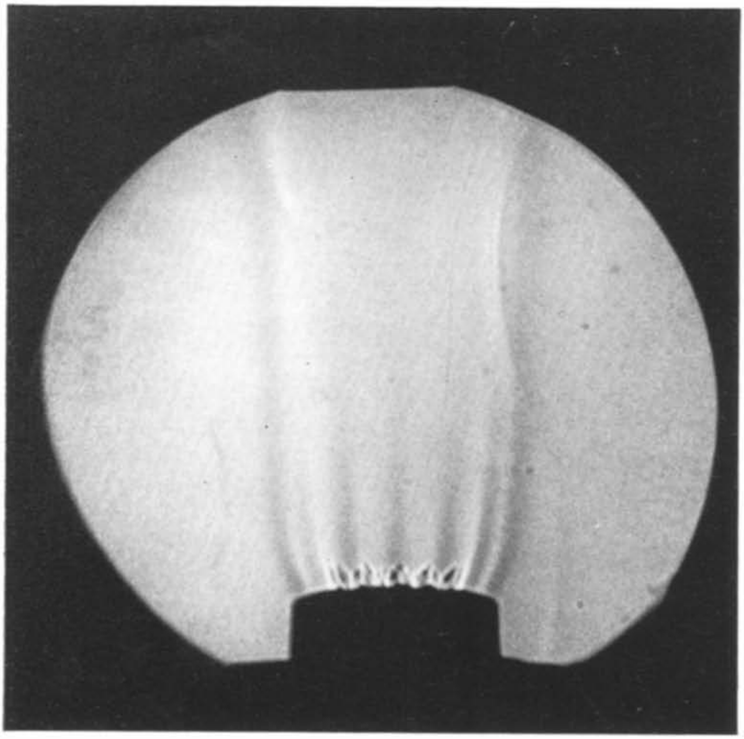
6

PLATES 5–6.—*Shadow and Schlieren records of fuel-rich air–acetylene flames.*

5. Schlieren photograph of separated flame (10 l./min N_2 flow) on capillary burner.
6. Shadowgram of normal flame on Beckmann RIIC burner.



7



8

PLATES 7–8.—*Shadow and Schlieren records of fuel-rich air–acetylene flames.*

7. Shadowgram of flame on Beckmann RIIC burner with 4 l./min N_2 for separation.
8. Shadowgram of flame on Beckmann RIIC burner with 10 l./min N_2 for separation.

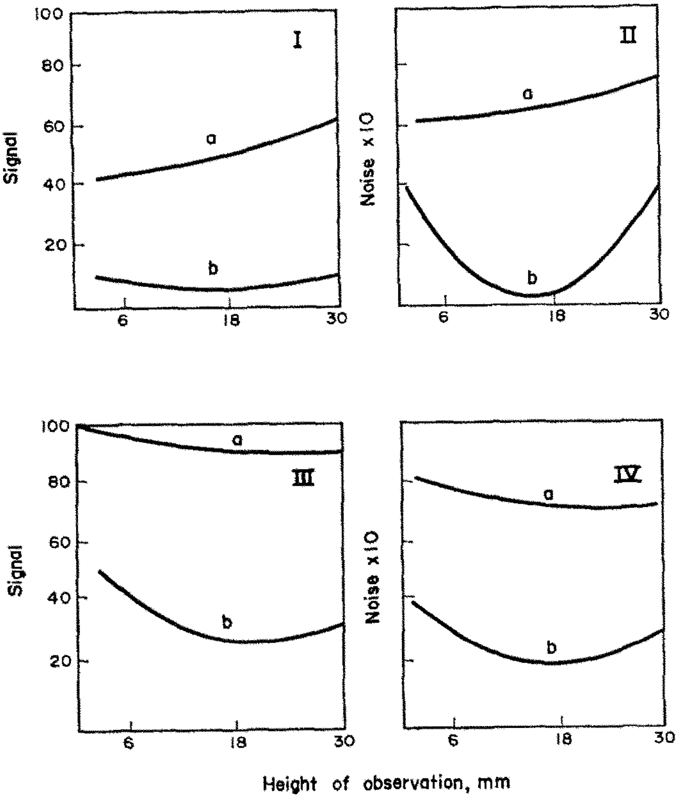


FIG. 4.—Variation of signal and noise with height. (*i*) OH emission, fuel-rich, (*ii*) OH emission noise, fuel-rich, (*iii*) OH emission, leaner flame, (*iv*) OH emission noise, leaner flame. *a*—No sheathing gas; *b*—6 l./min sheathing gas flow-rate.

regions at heights above 20 mm. The central flame regions appear to be relatively laminar.

The leaner air–acetylene flame is physically smaller and "stiffer" than the fuel-rich flame. Whatever turbulence is present, as indicated by the shadowgrams (not illustrated here), it varies little with height, whether the flame is unseparated or separated. Figures 4(*iii*) and (*iv*) confirm this behaviour in terms of the signals and their associated noise.

The effect of separation on the air–acetylene flame maintained on the Beckman RIIC burner is different from the effect when the flame is stabilized on a capillary burner. At a height of observation of 15 mm [Figs. 3(*iii*) and (*iv*)], the noise level actually increases at first as the nitrogen separation reduces the signal. The peak noise occurs at a flow-rate of 4 l./min. Plate 7 shows that at this flow there is a sharp delineation between the lower part of the flame, which is separated, and the part above it, which is unseparated, and where gases are burning. This transitional region occurs at a height of about 15 mm in the flame and of course leads to a noisy signal. The behaviour of the Beckman RIIC burner and separator should be contrasted with that of the capillary burner and separator. With this capillary arrangement, all flow-rates of nitrogen give progressive separation up the flame without any sharp boundaries between separated and unseparated regions.

Atomic-absorption signals. Copper is nearly completely atomized in the air–acetylene flame.[13] Therefore, the atomic-absorption signal from a copper solution nebulized into such a flame is a measure of the steady-state atomic concentration which lies in the radiative path between the atomic line source and the detector. Any fluctuations in the signal must then only reflect fluctuations in the local steady-state atomic concentration plus nebulizer noise, which will remain a constant proportion of the signal.

Figure 5(*iii*) shows the variation in copper atomic absorption with increasing nitrogen separation. As expected, the signal is negligibly altered. On separation at a flow-rate of 6 l./min of nitrogen the noise drops by a factor of 2. This confirms the previous deduction that separation at this flow rate not only reduces fluctuations in the outer flame mantle, but actually stabilizes the whole body of the flame. Again, separation at a flow-rate of 10 l./min causes turbulence, and the noise returns almost to its unseparated level, as with the OH emission.

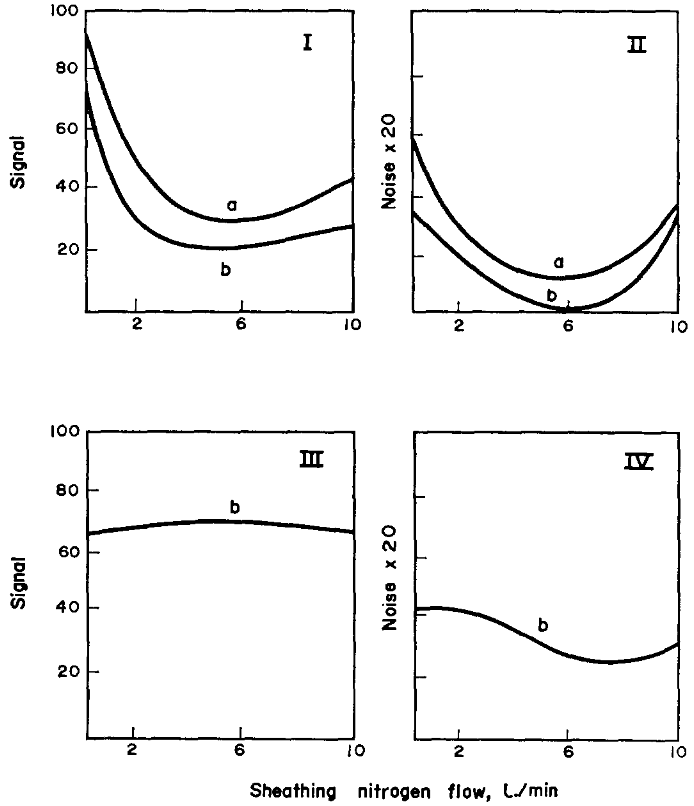


Fig. 5.—Copper atomic-absorption and emission at 324·1 nm.
(*i*) Cu emission signal. Lean flame
(*ii*) Cu emission noise. Lean flame
(*iii*) Cu atomic-absorption signal. Fuel-rich flame
(*iv*) Cu atomic-absorption noise. Fuel-rich flame.

Atomic-emission signals. The copper flame-emission signals in a lean air–acetylene flame are shown in Figs. 5(*i*) and (*ii*) in comparison with the OH emission in the same flame (the signals are scaled). Copper is assumed to have a β value of unity in this flame, so the copper emission magnitude is a measure of the temperature of the flame. With increased nitrogen flow the signal drops in almost exactly the same way as the OH emission. The drop in signal is equivalent to about a 10° drop in temperature of the whole flame. The noise observed, however, drops by a greater degree than does the OH noise.

Influence of other sources of turbulence. So far only turbulent phenomena in laminar flames with nitrogen sheaths have been considered. Although these have considerable application to atomic-fluorescence spectroscopy,[14] in other applications, *i.e.*, long-path atomic-absorption spectroscopy, separation may not be considered so advantageous. In these instances the laminarity of the *un*separated flame is of prime importance. In order to relate this to the analytical signal, atomic-absorption and flame-emission signals from copper in laminar flames were compared with the signals from the same flames when made turbulent by doubling the total gas supply to the burner. The acetylene:air ratio was maintained constant. The drop in signal in both atomic-absorption and flame-emission was slight, 2% and 7% respectively. However, the noise in both cases approximately doubled. Turbulence therefore gives rise to noise in unseparated flames in much the same way that it does in separated flames.

CONCLUSIONS

It has been shown by this study that optical methods provide valuable records of the combustion processes in premixed laminar flames. The optical disturbances which these photographs reveal may be interpreted in terms of the laminarity or turbulence of the flame gases, provided that the information is used on a well-defined comparative basis. From an analytical standpoint, the records are of value because they give insight into the processes which lead to variations in the magnitudes and noise levels of atomic-absorption (and hence atomic-fluorescence) and flame emission signals. The beneficial effect on signal noise of the correct level of nitrogen separation has been shown.

Of the two optical techniques examined, both of which require relatively inexpensive equipment, the shadow method has been shown to provide as much information as Schlieren photography whilst involving a simpler experimental arrangement, and so is to be preferred.

Zusammenfassung—Die Anwendung von Schlieren- und Schattenverfahren auf die Untersuchung von Vorgängen in Flammen wird im Hinblick auf die analytisch nützlichen vorgemischten Flammen diskutiert. Die besonders aus Schattenphotographien erhaltene Information kann zu den bei der Atomabsorptions- und Flammenemissionspektrometrie gemessenen Signalen und deren Rauschen in Beziehung gesetzt werden.

Résumé—On discute de l'application des techniques "Schlieren" et d'ombre pour l'étude des processus de flamme en relation avec les flammes prémélangées analytiquement utiles. Les informations obtenues, particulièrement avec les sciogrammes, peuvent être rattachées aux signaux mesurés et au bruit remarquable en spectrométrie d'absorption atomique et d'émission de flamme.

REFERENCES

1. F. J. Weinberg, *Optics of Flames*, Butterworths, London, 1963.
2. V. A. Fassel and D. W. Golightly, *Anal. Chem.*, 1963; **39**, 466.
3. W. Slavin, *At. Absorption Newsletter*, 1967, **6**, 9.

4. C. S. Rann, *Spectrochim. Acta*, 1968, **23B**, 827.
5. V. G. Mossotti and M. Duggan, *Appl. Opt.* 1968, **7**, 1325.
6. M. P. Bratzel, Jr., R. M. Dagnall and J. D. Winefordner, *International Atomic Absorption Spectroscopy Conference*, Sheffield, 1969.
7. S. Goldman, *Frequency Analysis Modulation and Noise*, p. 380. McGraw-Hill, New York, 1948.
8. J. D. Winefordner and T. J. Vickers, *Anal. Chem.*, 1964, **36**, 1939.
9. *Idem*, *ibid.*, 1965, **37**, 416.
10. *Idem*, *ibid.*, 1964, **36**, 1947.
11. J. D. Winefordner, M. L. Parsons, J. M. Mansfield and W. J. McCarthy, *ibid.*, 1967, **39**, 437.
12. K. M. Aldous, R. F. Browner, R. M. Dagnall and T. S. West, *ibid.*, 1970, **42**, 939.
13. L. de Galan and J. D. Winefordner, *J. Quant. Spectry. Radiative Transfer*, 1967, **7**, 251.
14. R. F. Browner and D. C. Manning, *Anal. Chem.* in press.

Talanta, 1972, Vol. 19, pp. 937 to 944. Pergamon Press. Printed in Northern Ireland

SELECTIVE EXTRACTION OF ZINC DITHIZONATE IN THE PRESENCE OF DITHIOCARBAMINOACETIC ACID AS MASKING AGENT

QUANTITATIVE TREATMENT OF AN EXTRACTION EQUILIBRIUM

O. BUDEVSKY, E. RUSSEVA and R. STOYTCHEVA
Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Sofia 13, Bulgaria

(*Received* 15 *October* 1971 *Accepted* 17 *November* 1971)

Summary—Dithiocarbaminoacetic acid (TCA) is proposed as an effective masking agent in the dithizone extraction determination of zinc in the presence of lead, cadmium and cobalt(II). The extraction equilibrium is treated quantitatively by means of two approaches: the "conditional distribution coefficient" and the computer program HALTAFALL. Both methods give similar results and enable the most suitable conditions for the separation and determination of zinc in the presence of the other ions to be determined. A successful attempt is made to predict the maximum permissible quantity of interfering elements. The experimental check, performed under various conditions, is in satisfactory agreement with the theory.

THE DETERMINATION of trace amounts of zinc in the presence of other elements and especially in the presence of cadmium and lead is a comparatively difficult analytical problem. The dithizone extraction method is useful for the isolation and determination of small amounts of metal ions, and the selectivity of the extraction equilibrium can be favourably shifted by means of suitable masking agents, such as dithiocarbamates. Margerum and Santacana[1] in a comparative study of the methods for determination of trace amounts of zinc, recommended the dithizone extraction method in the presence of bis (2-hydroxyethyl) dithiocarbamate, the latter having also been used by Galík.[2] Hulanicki[3,4] proposed bis(carboxymethyl) dithiocarbamate for similar purposes. Other investigations showed that dithiocarbaminoacetic acid (TCA) can be successfully used as a masking agent in the complexometric determination of zinc in the presence of lead, cadmium, nickel and cobalt(II).[5] There is a difference of 3–4 logarithmic units between the stability constants of zinc–TCA complexes and the TCA complexes of other metal ions (see Table I).[6–10] The extraction constant of zinc dithizonate is the highest for any dithizonate. These factors together suggest that it should be possible to find conditions for the selective extraction of zinc dithizonate in the presence of TCA as a masking agent and this was the first aim of the present investigation. The behaviour of other metal ions in this extraction cannot be predicted by general considerations, since their extraction constants are generally 5–6 logarithmic units higher than the stability constants of the corresponding TCA complexes, but it should be possible to compute the most favourable conditions for this determination from a quantitative treatment of the appropriate equilibria. The second aim of the present investigation was to compute the optimum conditions and the third aim was to test the validity of the calculations against experimental evidence.

METHODS OF CALCULATION

The solvent extraction problem, like many others, can be reduced to the calculation of the distribution coefficients of the different ions as a function of several factors. Many authors, from Irving, Rossotti and Williams onward,[11-15] have treated extraction equilibria quantitatively, but it seems at the present moment that two approaches are most convenient. One of them, developed by Ringbom and Still,[16] is based on the concept of the "conditional equilibrium constant" and uses several approximations in the course of the calculations. The second one, proposed by Sillén and co-workers,[17] gives an exact solution of the problem by using the multipurpose computer program HALTAFALL.

Both methods were examined in this study and therefore some specific details of the application of these methods will be briefly discussed.

Method of calculation based on the concept of conditional distribution coefficient

The fundamental principles of the concept will not be stated here, because they are comprehensively dealt with in Ringbom's book[18] but because the equation for the conditional distribution coefficient used in the present paper is not derived in that book, its derivation will be shortly discussed.

The conditional distribution coefficient, the most important in a particular analysis, is defined as a ratio between the total concentration of the metal, whatever its form, in the organic and aqueous phases (symbols used are the same as those in ref 18)

$$D' = \frac{\text{Total concentration of the metal in the organic phase}}{\text{Total concentration of the metal in the aqueous phase}} = \frac{[\mathrm{M}']_0}{[\mathrm{M}']} \qquad (1)$$

Simplifications in (1) can be made when some chelates (*e.g.* dithizonates) are extracted, if it is assumed that the only form of the metal ions present in the organic phase is the uncharged chelate MR_n. Then

$$D' = \frac{[\mathrm{MR}_n]_0}{[\mathrm{M}']} \qquad (1')$$

On the other hand, extraction equilibria of chelates are quantitatively described by the extraction constant

$$E_{\mathrm{MR}_n} = \frac{[\mathrm{MR}_n]_0}{[\mathrm{M}][\mathrm{R}]^n} \qquad (2)$$

but when interferences are present (e.g. acidity of the solution, the presence of masking agents *etc*) a convenient way to take into consideration the side-reactions that can occur in the system is to introduce the overall α-coefficients and the conditional extraction constant

$$E'_{\mathrm{MR}_n} = \frac{[\mathrm{MR}_n]_0}{[\mathrm{M}'][\mathrm{R}']^n} = \frac{E_{\mathrm{MR}_n}}{\alpha_{\mathrm{M}}\alpha_{\mathrm{R}}^{\,n}} \qquad (3)$$

A substitution of (1′) in (3) gives the equation of the conditional distribution coefficient

$$D' = \frac{E_{\mathrm{MR}_n}[\mathrm{R}']^n}{\alpha_{\mathrm{M}}\alpha_{\mathrm{R}}^{\,n}} \qquad (4)$$

or in its logarithmic form

$$\log D' = \log E_{\mathrm{MR}_n} + n \log \mathrm{R}' - \log \alpha_{\mathrm{M}} - n \log \alpha_{\mathrm{R}} \qquad (4')$$

The overall α-coefficients introduced in (3) and (4) will be discussed more closely.

α_{R} is calculated on the basis of considerations that have been thoroughly discussed by Ringbom.[18] Further it is assumed that microgram amounts of zinc will be extracted, so a sufficient excess of dithizone would be provided by a $10^{-4}M$ solution. The volumes of the organic and aqueous phase are taken as equal (10 ml).

α_{M} is the overall α-coefficient taking into consideration the side-reactions of the metal ions in the aqueous phase. Two side-reactions can be considered: (*i*) the reaction of the metal ion with TCA and (*ii*) the formation of hydroxo-complexes, hence

$$\alpha_{\mathrm{M}} = \alpha_{\mathrm{M(TCA)}} + \alpha_{\mathrm{M(OH)}} - 1 \qquad (5)$$

At pH 9 the value of $\alpha_{\mathrm{M(OH)}}$ for zinc, lead, cadmium, cobalt(II) and nickel can be neglected (see ref. 18, Table A.5, p. 353) and α_{M} is given by (*cf.* ref. 19)

$$\alpha_{\mathrm{M}} \sim \alpha_{\mathrm{M(TCA)}} = \sum \beta_n \frac{[\mathrm{TCA}']^n}{\alpha^n_{\mathrm{TCA(H)}}} \qquad (6)$$

where the β_n values are the corresponding stability constants of zinc and the other metal ions with TCA; [TCA′] is the total concentration of dithiocarbaminoacetic acid not bound to the main metal ion and $\alpha_{\mathrm{TCA(H)}}$ is the α-coefficient of TCA taking into consideration the protonation of the ligand. $\alpha_{\mathrm{TCA(H)}}$ is calculated as a function of pH according to

$$\alpha_{\mathrm{TCA(H)}} = 1 + \beta_1{}^{\mathrm{H}}[\mathrm{H}] + \beta_2{}^{\mathrm{H}}[\mathrm{H}]^2 \qquad (7)$$

where $\beta_1{}^{\mathrm{H}}$ and $\beta_2{}^{\mathrm{H}}$ are the overall proton stability constants of TCA.

TABLE I.—EQUILIBRIUM CONSTANTS USED IN THE PRESENT PAPER

Dithizone extraction constants in CCl_4[18]		Constants for dithizone[18]	
$\log E_{\mathrm{ZnR_2}} = 19{\cdot}3$		$\mathrm{p}K_{\mathrm{H}} = 4{\cdot}5$	
$\log E_{\mathrm{CdR_2}} = 18{\cdot}8$		$\log D_{\mathrm{HR}} = 4{\cdot}0$ (CCl_4)	
$\log E_{\mathrm{PbR_2}} = 17{\cdot}7$		$\mathrm{pH}_{1/2} = 8{\cdot}5$	
$\log E_{\mathrm{CoR_2}} = 18{\cdot}6$			
$\log E_{\mathrm{NiR_2}} = 16{\cdot}2$			
Constants for TCA[6-10]			
H^+	$\log \beta_1{}^{\mathrm{H}} = 3{\cdot}7$	$\log \beta_2{}^{\mathrm{H}} = 6{\cdot}7$	
Zn^{2+}	$\log \beta_1 = 3{\cdot}4$	$\log \beta_2 = 6{\cdot}5$	$\log \beta_3 = 9{\cdot}1$
Cd^{2+}	$\log \beta_1 = 5{\cdot}4$	$\log \beta_2 = 9{\cdot}3$	$\log \beta_3 = 13{\cdot}6$
Pd^{2+}	$\log \beta_1 = 7{\cdot}3$	$\log \beta_2 = 13{\cdot}1$	
Co^{2+}	$\log \beta_1 = 3{\cdot}3$	$\log \beta_2 = 7{\cdot}8$	$\log \beta_3 = 13.3$
Ni^{2+}		$\log \beta_2 = 8{\cdot}5$	

The calculations of the α-coefficients and the conditional distribution coefficients were performed with the set of stability constants shown in Table I. In Table II are shown the calculated values of the α-coefficients and the conditional distribution coefficients according to (4′) for zinc, cadmium and lead dithizonates. The values of $\log D'_{\mathrm{MR}_2}$ from Table II are drawn in Fig. 1 with a full line and will be discussed later.

Table II.—Values of calculated α-coefficients and conditional distribution coefficients computed with equations (7), (6) and (4′) for zinc, cadmium and lead

pH	$\log \alpha_{\mathrm{TOA(H)}}$	$2\log \alpha_{\mathrm{R}}$	$\log \alpha_{\mathrm{Zn}}$	$\log \alpha_{\mathrm{Cd}}$	$\log \alpha_{\mathrm{Pb}}$	$\log D'_{\mathrm{Z}\ \ 2}$	$\log D'_{\mathrm{CdR_2}}$	$\log D'_{\mathrm{PbR_2}}$
3	1·05	11·0	3·0	7·5	9·0	−3·7	−7·7	−10·3
4	0·20	9·0	5·6	10·0	10·7	−3·3	−8·2	−10·0
5	0·02	7·0	6·0	10·5	11·1	−1·7	−6·7	−8·4
6	—	5·0	6·1	10·6	11·1	+0·2	−4·8	−6·4
7	—	3·0	6·1	10·6	11·1	+2·2	−2·8	−4·4
8	—	1·2	6·1	10·6	11·1	+4·0	−1·0	−2·6
9	—	0·2	6·1	10·6	11·1	+5·1	±0·0	−1·6

$C_{\mathrm{TCA}} = 0{\cdot}1M$; $C_{\mathrm{H_2Dz}} = 10^{-4}M$; $V_{\mathrm{org}} = V_{\mathrm{aq}} = 10$ ml.

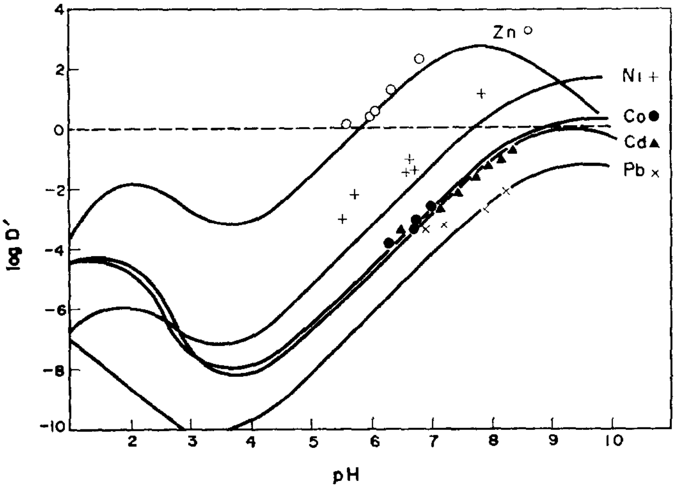


Fig. 1.—pH-dependence of logarithm of distribution coefficient of dithizonates in the presence of TCA.

Analogous calculations with 0·01M and 0·05M TCA solutions were performed but no advantage was found: the family of curves shown in Fig. 1 is shifted towards lower pH values without change in their mutual position. Therefore it is considered that 0·1M TCA solution is more suitable for a masking procedure as it is easier for preparation in analytical work; moreover such a solution is less sensitive to unexpected influences.

Computer method of calculation

The method of Sillén uses high-speed computers and the program HALTAFALL to resolve a system of mass-balance equations of the components, provided that the equilibrium constants of the complexes and the total concentrations of the components are known. The HALTAFALL program is flexible and can be used in many fields of chemistry dealing with homogenous and heterogenous equilibria, including extraction. The input for the program was made for the same conditions as these used in the foregoing calculations. As an illustration Table III gives the input and output from the calculations for cadmium dithizonate in the presence of TCA, as performed on the Danish GIER computer. More details of writing the input for HALTAFALL can be found in the original paper[17] or in the monograph by Dyrssen *et al.*[20]

TABLE III.—INPUT AND OUTPUT FROM HALTAFALL PROGRAM FOR THE CALCULATION OF DISTRIBUTION OF CADMIUM DITHIZONATE IN PRESENCE OF TCA. SOME EXPLANATIONS ARE GIVEN IN BRACKETS

```
Input
 0,0, Distribution of cadmium(II)-Dithizonate in presence of TCA
 5,                                                              (Number of components)
 −11, 0,                                                         (Number of complexes)
 (the constants)    (Cd      TCA      H      Dz      Fas2)

 1·00, −14,          0,       0,      −1,     0,      0,         (OH)
 2·51,   5,          1,       1,       0,     0,      0,         (Cd(TCA))
 2·00,   9,          1,       2,       0,     0,      0,         (Cd(TCA)_2)
 3·98,  13,          1,       3,       0,     0,      0,         (Cd(TCA)_3)
 5·00,   3,          0,       1,       1,     0,      0,         (HTCA)
 5·00,   6,          0,       1,       2,     0,      0,         (H_2TCA)
 6·31, −11,          1,       0,      −1,     0,      0,         (CdOH)
 7·94, −10,          1,       0,      −2,     0,      0,         (Cd(OH)_2)
 1·58, −32,          4,       0,      −4,     0,      0,         (Cd_4(OH)_4)
 3·16,   8,          0,       0,       1,     1,      1,         (HDz_0)
 6·31,  18,          1,       0,       0,     2,      1,         (((Cd(Dz)_2)_0)
 0, 3, −3, 2, −1, 6, −1, 7,                                      (printing orders)
 1, 0·2, 10, 1, −15, 1_10 −8, 1_10 −6,                           (data for concentration
 1, −1, 1_10 −5, 1_10 −1,6, −1, −1, 1, −6, 1_10 −5, 1_10 −4      of the components)

Output — first line from calculations
      LOG A 3             LOG D 1           D/(1 + D) 1      (pH,log D'_CdR_2, %E10^-2)
     −1·000000          −4·406258           0·000039
     −2·000000          −4·861752           0·000014
     −3·000000          −7·644097           0·000000
     −4·000000          −8·227364           0·000000
     −5·000000          −6·707334           0·000000
     −6·000000          −4·822125           0·000015
     −7·000000          −2·874154           0·001334
     −8·000000          −1·029517           0·085446
     −9·000000          −0·061787           0·464492
    −10·000000          −0·311633           0·327930
```

Choice of conditions for the selective extraction of zinc dithizonate

The starting point in the choice of conditions for the selective extraction of zinc dithizonate must be the analysis of the distribution coefficient of zinc and the other ions as a function of pH as well as of other variables. From Fig. 2, where the calculated degree of extraction of the dithizonates is plotted it can be seen that in the absence of TCA no separation of zinc from the other ions is possible. In the presence of TCA, however, the same figure shows that at pH 6·5–7·0 zinc can be selectively extracted.

Furthermore, it is found that the calculations can be used for the quantitative evaluation of the maximum permissible amount of interfering ions. From the curves plotted in Fig. 1, the lowest pH value can be found for satisfactory extraction of zinc, viz. pH = 6·8. At this pH value the distribution coefficient is $\log D'_{\mathrm{ZnR_2}} = 1{\cdot}7$, corresponding to a *ca.* 98% extraction of zinc. At the same pH value the extraction of the other ions is given by $\log D'_{\mathrm{NiR_2}} = -1{\cdot}8$, $\log D'_{\mathrm{CoR_2}} = -3{\cdot}2$ $\log D'_{\mathrm{CdR_2}} = -3{\cdot}3$ and $\log D'_{\mathrm{PbR_2}} = -4{\cdot}7$. Using the molar absorptivities of the dithizonates at 530 nm and the distribution coefficients mentioned, the quantity of foreign ions can be calculated (as shown in Table IV), that will produce interference in the organic phase equal to +0·1 μg of zinc.

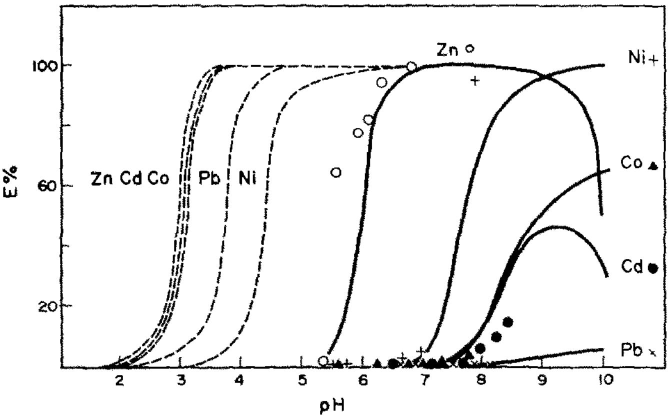


FIG 2.—pH-dependance of degree of extraction of dithizonates in the presence (———) and in the absence (— — —) of TCA.

TABLE IV.—CALCULATIONS OF MAXIMUM PERMISSIBLE QUANTITY OF INTERFERING IONS WITH THE DITHIZONE EXTRACTION OF 1 μg OF ZINC

Metal ion	ε, Molar absorptivity of dithizonates at 530 nm*	Ratio $\varepsilon_{Zn/Me}$	Ratio of atomic weights Me/Zn	Interference of unit weight of metal per weight unit of Zn	Amount of interfering metal equivalent to 0·1 μg of Zn	$D'_{pH=6\cdot8}$ of metal dithizonates	Permissible maximum quantity of interfering ion μg
Zn^{2+}	92·0						
Cd^{2+}	88·0	1·04	1·72	1·79	0·18	$5\cdot01 \times 10^{-4}$	360
Co^{2+}	59·2	1·55	0·90	1·40	0·14	$6\cdot31 \times 10^{-4}$	220
Pb^{2+}	68·8	1·34	3·16	4·24	0·42	$2\cdot00 \times 10^{-4}$	2100
Ni^{2+}	*ca.*17·0†	5·41	0·90	4·88	0·49	$1\cdot58 \times 10^{-2}$	31

* Data from Iwantschew,[21] Table 5, p. 40.

† Recalculated from Iwantschew,[21] Fig. 36, p. 279.

EXPERIMENTAL

Reagents

Dithizone solution, $10^{-3}M$. Reagent grade dithizone (0·0256 g) was dissolved in 100 ml of carbon tetrachloride. After tenfold dilution the dithizone concentration was checked by extraction titration with standard silver nitrate solution.[21]

Diammonium dithiocarbaminoacetate monohydrate, ($NH_4SCSNHCH_2COONH_4 \cdot H_2O$). Prepared and kept according to ref. 5.

Carbon tetrachloride. Purified and distilled.[21]

Stock solutions of zinc, lead, cadmium, cobalt(II) and nickel were standardized complexometrically and then diluted.

Water. Twice distilled from a quartz still and kept in Teflon vessels.

In the light of the chosen conditions, the experiments were performed with two objectives: (*i*) estimation of distribution coefficients of the dithizonates as a function of pH at constant TCA concentration and (*ii*) evaluation of maximum permissible amount of interfering element in the determination of zinc.

The distribution coefficients of the dithizonates was determined spectrophotometrically from the difference of the metal ion content in the organic phase and the total amount. With zinc the total was 4 μg, while with the other ions the total was increased (cadmium up to 900 μg, lead up to 5000 μg etc). For higher metal ion concentrations, a corresponding correction in the total of TCA was made, ensuring 0·1M free TCA concentration.

TABLE V.—DETERMINATION OF 1·00 μg OF ZINC IN THE PRESENCE OF DIFFERENT AMOUNTS OF INTERFERING ELEMENTS (pH = 6·8, 0·1M TCA)

Cd taken, μg	Zn found μg	Pb taken, μg	Zn found, μg	Co taken, μg	Zn found, μg	Ni taken, μg	Zn found, μg
100	0·99	500	1·03	50	1·00	1·00	0·95
	1·10		1·18				0·90
	0·95						
200	1·00	1000	1·13	100	1·05	2·00	0·92
	1·06		1·06				
	1·00		0·90				
500	1·17	2000	1·01	200	1·08	4·00	1·03
	1·15		1·15		1·05		1·03
	1·15		1·06		1·12		
1000	1·10	3000	1·06	500	1·05	6·00	1·17
	1·12				1·15		1·20
		5000	1·03	600	1·15		
			0·90		1·20		
		10000	1·18	1000	2·40		
			1·25				
			2·65				

Procedure

Aqueous phase (10 ml), containing a definite quantity of metal ion, 0·2 g of TCA (0·1M), adjusted to pH 6·8 before extraction and checked afterwards, was extracted with 10 ml of $10^{-4}M$ dithizone solution in carbon tetrachloride. After separation, the organic phase was washed twice with 10 ml of 0·01M ammonia. The absorbance of the washed extract was measured at 530 nm in a 2-cm cell against a blank. The quantity of metal ion was obtained from a calibration curve.

For the determination of the maximum permissible amount of interfering element, the extraction was performed in the same manner, except that a (phosphate) buffer was added and a constant amount of zinc was used.

The experimental results are plotted in Figs. 1 and 2 and given in Table V, and coincide satisfactorily with the theory.

DISCUSSION

Dithiocarbaminoacetic acid serves as an effective masking agent for the dithizone extraction and determination of zinc in the presence of lead, cadmium and cobalt (II). As lead and cadmium normally cause grave interferences, TCA could serve as an useful masking agent in the development of methods for the determination of trace amounts of zinc.

It is shown that by calculation the most suitable conditions can be predicted for an extractive analytical procedure for the separation and determination of one component in the presence of others. This is illustrated in Fig. 2, where at pH 6·5–7·0 a separation and determination of zinc in the presence of lead, cadmium, cobalt(II) and nickel is seen to be possible. The experimental check performed in the presence of TCA is in good agreement with the theory. It is obvious also that in the absence of TCA no separation can be realized.

A successful attempt was made to predict the maximum permissible quantity of interfering elements in the dithizone determination of zinc in the presence of TCA, *e.g.*, for cadmium the predicted ratio Zn:Cd is 1:360 and the experimental ratio is 1:200. Some discrepancies found for lead and nickel can be explained by the low value of the distribution coefficient of the former, and insufficient accuracy of some of the equilibrium constants used for the latter.

Both methods of calculation used give similar results and are in good agreement with experiment but it seems that the HALTAFALL method is less time-consuming and is more exact.

Zusammenfassung—Dithiocarbaminoessigsäure (TCA) wird als wirksams Maskierungsmittel bei der Bestimmung von Zink in Gegenwart von Blei, Cadmium und Kobalt(II) durch Extraktion mit Dithizon vorgeschlagen. Das Extraktions-Gleichgewicht wird auf zwei Arten quantitativ behandelt: unter Verwendung des "konzentrationsbedingten Verteilungskoeffizienten" und mit dem Rechnerprogramm HALTAFALL. Beide Methoden geben ähnliche Ergebnisse und geben die Möglichkeit, die für die Abtrennung und Bestimmung von Zink in Gegenwart der anderen Ionen am besten geeigneten Bedingungen zu ermitteln. Es wird ein erfolgreicher Versuch unternommen, die höchste zulässige Menge an störenden Elementen vorauszusagen. Die Überprüfung durch das Experiment stimmt unter verschiedenen Bedingungen zufriedenstelland mit der Theorie überein.

Résumé—On propose l'acide dithiocarbaminoacétique (TCA) comme agent de dissimulation efficace dans le dosage par extraction à la dithizone du zinc en la présence de plomb, cadmium et cobalt(II). L'équilibre à l'extraction est traité quantitativement par deux voies: le "coefficient de partage conditionnel" et le programme de calculatrice HALTAFALL. Les deux méthodes donnent des résultats similaires et rendent possible la détermination des conditions les plus convenables pour la séparation et le dosage du zinc en la présence des autres ions. On a fait un essai réussi de prédiction de la quantité maximale admissible d'éléments gênants. Le contrôle expérimental, réalisé dans diverses conditions, est en accord satisfaisant avec la théorie.

REFERENCES

1. D. W. Margerum and F. Santacana, *Anal. Chem.*, 1960, **32**, 1157.
2. A. Galík, *Talanta*, 1967, **14**, 731.
3. A. Hulanicki, *Chem. Anal. (Warsaw)*, 1966. **11**, 1081.
4. A. Hulanicki and M. Minczewska, *Talanta*, 1967, **14**, 677.
5. O. Budevsky, E. Russeva and B. Mesrob, *ibid.*, 1966, **13**, 277.
6. O. Budevsky and E. Russeva, *Mitt. Inst. Allg. Anorg. Chem. Bulg. Ak. Wiss.*, 1966, **4**, 5.
7. O. Budevsky and O. Zakharieva, *ibid.*, 1966, **4**, 15.
8. O. Budevsky and E. Platikanova, *Talanta*, 1967, **14**, 901.
9. O. Budevsky, E. Russeva and T. Sotyrova, *ibid.*, 1968, **15**, 629.
10. O. Budevsky and O. Zakharieva, unpublished results.
11. H. Irving, F. Rossotti and R. J. P. Williams, *J. Chem. Soc.*, 1955, 1906.
12. G. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry* (Russ. Transl.), p. 58. Goskhimizdat, Leningrad, 1960.
13. H. A. Laitinen, *Chemical Analysis* (Russ. Transl.), Khimia, Moscow, 1966.
14. H. Freiser and Q. Fernando, *Ionic Equilibria in Analytical Chemistry*, Wiley, New York, 1963.
15. J. Starý, *The Solvent Extraction of Metal Chelates* (Russ. Transl.), MIR, Moscow, 1966.
16. A. Ringbom and E. Still, *Finska Kemistsamfundets Medd.*, 1960, **69**, 17.
17. N. Ingri, W. Kakolowicz, L. G. Sillén and B. Warnqvist, *Talanta*, 1967, **14**, 1261.
18. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
19. G. Schwarzenbach and H. Flaschka, *Die Komplexometrische Titration*, 5th Ed., p. 105, eq. (69). Enke, Stuttgart, 1965.
20. D. Dyrssen, D. Jagner and F. Wengelin, *Computer Calculation of Ionic Equilibria and Titration Procedures*, Almkvist & Wiksell, Stockholm; Wiley, New York, 1968.
21. G. Iwantscheff, *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse* (Russ. Transl.), Izdanlit, Moscow, 1961.

Talanta, 1972, Vol. 19, pp. 945 to 952. Pergamon Press. Printed in Northern Ireland

NIEDERSCHLAGSBILDUNG—III

KRISTALLWACHSTUM UND EINFLUSS DER FREMDIONENKONZENTRATION IN DER BARIUMSULFATFÄLLUNG

CANDIN LITEANU und HARALD LINGNER
Lehrstuhl für Analytische Chemie der Universität von Cluj-Rumänien

(*Eingegangen am* 20. *April* 1971. *Angenommen am* 4. *Dezember* 1971)

Zusammenfassung—Es wurde sedimentometrisch der Einfluß von Fremdionen auf die Korngrösse der Bariumsulfatniederschläge bestimmt und festgestellt, daß bei großen Konzentrationen von NaCl, $NaNO_3$, KBr, KNO_3 u.a. auch bei großen Übersättigungsgraden das Wachstum der Kristalle stark gehemmt ist. Die lineare Wachstumsgeschwindigkeit wurde in Abhängigkeit von der $BaSO_4$-Konzentration, der Fremdionenkonzentration und des Verhältnisses $[BaCl_2]/[K_2SO_4]$ untersucht. Da schon bei fünffacher Übersättigung das Wachstum diffusionsbestimmt ist, können Bariumsulfatniederschläge keine Ostwaldreifung aufweisen. Für die Wachstumsbestimmungen wurde eine entsprechende Versuchseinrichtung gebaut.

IN ZWEI vorherigen Arbeiten[1,2] wurde der Einfluß verschiedener Faktoren auf die Bariumsulfatfällung mit Hilfe der Sedimentationsanalyse untersucht. Dieselbe Methode wurde benutzt, um den Einfluß einiger Salze wie NaCl, KCl, KNO_3, KBr, KJ, CH_3COONa u.a. auf die Korngröße des Bariumsulfatnierschlages zu bestimmen. La Mer und Dinegar[3] haben gezeigt, daß besonders die Nitrationen stark an der Oberfläche adsorbiert werden und daß in Gegenwart von Fremdionen der Übersättingungsgrad stark fällt. Die Adsorbtion einiger Ionen wie Diphosphat[4] oder Farbstoffen[5,6] können das Kristallwachstum völlig verhindern. Es wurde festgestellt, daß der mittlere Kornradius $\bar{r}$ (Stokesscher Radius) stark von der Konzentration der Fremdionen abhängt, wie Abb. 1 zeigt.

Ähnliche Resultate erhält man auch mit allen anderen oben angeführten Salzen. Eine Erklärung dafür wäre der geringere Übersättingungsgrad in diesem Falle. Da für einen Niederschlag C_mA_n das Löslichkeitsprodukt gegeben ist durch

$$K_S = c_A{}^n \cdot c_C{}^m = \frac{K_a}{\gamma_A{}^n \cdot \gamma_C{}^m} = \frac{K_a}{\gamma_\pm^{m+n}}$$

wo c_C und c_A die Konzentration der Ionen, γ_A und γ_C die entsprechenden Aktivitätskoeffizienten und $\gamma_\pm$ der mittlere Aktivitätskoeffizient bedeuten, K_a konstant bleibt und $\gamma_\pm$ mit steigender Ionenkonzentration fällt, so ist das Löslichkeitsprodukt in Gegenwart von Fremdionen größer als in Abwesenheit. Für den Aktivitätskoeffizienten gilt, wie bekannt, nach Hückel[7]:

$$-\log \gamma_\pm = \frac{z_A \cdot z_C A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} + C\mu,$$

A, B, C, Konstanten sind, a der mittlere Ionenradius, μ die Ionenstärke und z_A, z_C die Ionenladung bedeuten.

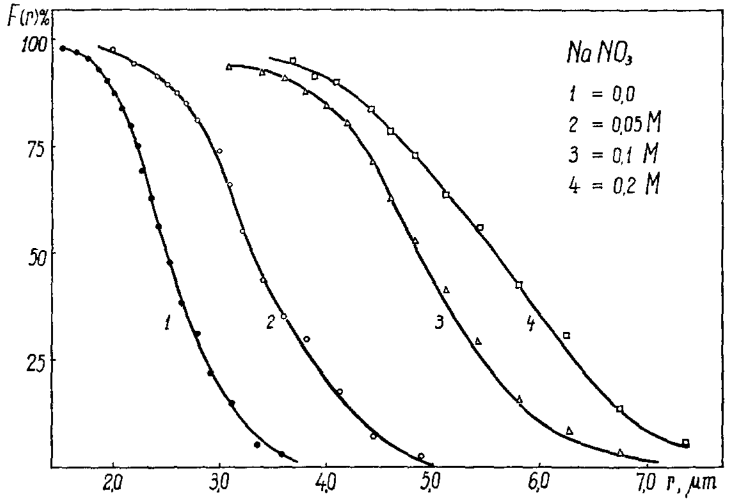


ABB. 1.—Einfluß der Natriumnitratkonzentration auf die Korngrößeverteilung bei Bariumsulfat.

Der Stokessche Radius wächst aber nicht gleichförmig mit wachsender Fremdionenkonzentration, da die Kristalle ihre Form nicht beibehalten. Trotz kleineren Abmessungen haben die in konzentrierten Lösungen erhaltenen Kristalle einen größeren Stokesschen Radius, da sie regelmäßigere Formen haben und ihre Fallgeschwindigkeit deshalb groß ist. Bei großen Fremdionenkonzentrationen wird die Niederschlagsbildung gehemmt; bei Konzentrationen größer als 0,1–0,2*M* bilden sich die meisten Kristalle an den Gefäßwänden. Scheinbar können sich in diesen Bedingungen in der Lösung keine Keime bilden, oder werden sie aufgelöst. Ähnliche Resultate wurden auch im Falle des Magnesiumammoniumphosphates erhalten.[8] In sehr konzentrierten Lösungen, zum Beispiel in gesättigten Natriumnitrat-oder Kaliumnitratlösungen, ist die Bildung des Niederschlages sogar bei Übersättigungsgraden über 100 auch nach Stunden nicht nachweisbar (in ungerührten Lösungen). Die Form der Bariumsulfatkristalle ändert sich in Gegenwart von Fremdionen bei allen untersuchten Übersättigungsgraden. Um zu bestimmen, ob die Adsorbtion oder eine Änderung des Wachstumsmechanismus die Formveränderung hervorruft, wurden die linearen Wachstumsgeschwindigkeiten unter verschiedenen Bedingungen gemessen. Im gegebenen Falle konnten natürlich keine Leitfähigkeitsmessungen durchgeführt werden und so wurde die Verschiebung einer Kristallfläche mikroskopisch verfolgt. Um während der Dauer der Bestimmung bei konstanter Konzentration zu arbeiten, wurde der in Abb. 2 wiedergegebene Apparat benutzt.

Auf eine farblose, durchsichtige Kunstoffplatte wurde eine kleine Schnellmischkammer *4* mit dem Einflußröhrchen *1,2* und dem Austrittsröhrchen *3* aufgekittet. Die im Verhältnis 1 :1 gemischten Bariumchlorid- und Kaliumsulfatlösungen strömen durch den mit einem Mikroskopdeckgläschen *6* abgedeckten Raum *5*. Werden die auf der Innenseite des Deckgläschens gebildeten Kristalle nach bestimmten Zeitintervallen fotografiert, so kann die lineare Wachstumsgeschwindigkeit leicht berechnet werden. Die Vorteile dieser Methode bestehen darin, daß dieselben Kristalle während

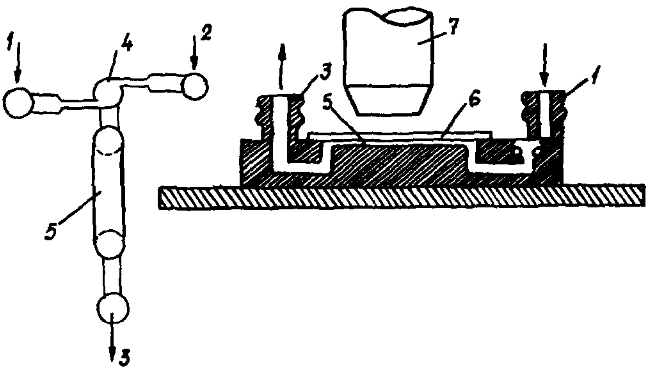


Abb. 2.—Apparat zur Bestimmung der linearen Wachstumsgeschwindigkeit. Es bedeuten:
1, 2 Einflußrohre für $BaCl_2$—und K_2SO_4—Lösung; 3 Abflußrohr; 4 Durchmischungskammer; 5 Meßraum; 6 Deckglas; 7 Mikroskop.

der ganzen Wachstumsperiode verfolgt werden und daß die Bariumsulfatkonzentration konstant gehalten wird. Die Durchflußgeschwindigkeit muß natürlich konstant gehalten werden, um vergleichbare Resultate zu erhalten.

Bei kleinen Übersättigungsgraden, ungefähr 10, ist die Wachstumsgeschwindigkeit sehr klein, es bilden sich stundenlang keine Kristalle auf dem Deckglas. Deshalb werden Kristalle durch Eintrocknen einer Suspension auf das Deckglas gebracht und es wird das Wachstum dieser Kristalle verfolgt. Am besten eignen sich dazu Kristalle, die durch Vermischen einer $4{,}10^{-4}M$ Bariumchloridlösung mit einer Kaliumsulfatlösung derselben Konzentration erhalten wurden, da sie regelmäßige Formen haben. Das Deckglas wird mit einer Mischung von Wachs und Kolophonium auf die Kunststoffplatte geklebt.

Ist die Diffusion wachstumsbestimmend, so wächst der Radius eines kugelförmigen Kristalles nach Neumann's[9] Gleichung;

$$r(t) = [2DV(c - c_s)t]^{1/2}$$

Ist die Grenzflächenreaktion Wachstumsbestimmend, so gilt

$$r(t) = kV(c - c_s)t$$

Hier bedeuten V das Molvolumen, D der Diffusionskoeffizient, c und c_s die Konzentration der Lösung bzw. die Sättigungskonzentration und t die Zeit.

Im Falle des Bariumsulfates erhält man Geraden, wenn man $r(t) = f(t^{1/2})$ graphisch darstellt, und zwar bei Konzentrationen über $5{,}10^{-5}M$. Bei kleineren Konzentrationen konnte auch nach 8 Stunden kein Wachstum festgestellt werden. Die Diffusion kann also schon bei einer fünffachen Übersättigung hemmend wirken. Dieser Wert ist fast um eine Größenordnung kleiner als der von Nielsen[10,11] gefundene. Kahlweit[12] hat festgestellt, daß TlJ äußerst langsam wächst, wenn die Konzentration nahe der Sättingungskonzentration liegt.

Stellt man die Länge der Bariumsulfatkristalle in Abhängigkeit von der Quadratwurzel der Zeit $\sqrt{t}$ graphisch dar, so erhält man für verschiedene Ausgangskonzentrationen wie in Abb. 3 dargestellte Geraden. Es wurden für jede Konzentration wenigstens 10 Kristalle gemessen. Unter denselben Versuchsbedingungen erhält man für jeden Kristall eine Gerade; diese sind parallel, aber gegeneinander verschoben, da für jeden Kristall eine bestimmte Induktionsperiode nötig ist. Diese Unterschiede sind jedoch nicht groß.

Da unter gegebenen Bedingungen $(c - c_s)$ konstant bleibt, kann Neumann's Gleichung geschrieben werden:

$$r(t) = K \cdot t^{1/2}$$

wo

$$K = [2DV(c - c_s)]^{1/2}$$

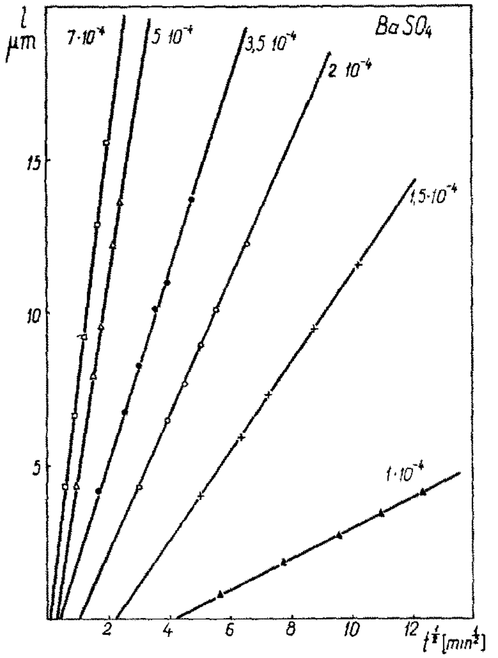


Abb. 3.—Einfluß der Bariumsulfatkonzentration auf die lineare Wachstumsgeschwindigkeit.

Aus der Neigung der Geraden kann also der Diffusionskoeffizient berechnet werden. Da aber die Kristalle stark von der Kugelform abweichen, müß ein Korrektionsfaktor bestimmt werden. So erhält man für die in Abb. 3 dargestellten Fälle Werte zwischen $2{,}4 \cdot 10^{-6}$ und $7{,}5 \cdot 10^{-6}$ cm² sec⁻¹, Werte die mit denen von Nielsen[11] aus Leitfähigkeitsmessungen erhaltenen ziehmlich gut übereinstimmen. Die für Konzentrationen unter $1 \cdot 10^{-4}M$ erhaltenen Werte sind jedoch kleiner, da in diesem Falle wahrscheinlich ein Zusammenspiel der Grenzflächenreaktion und der Diffusion vorliegt.

Aus diesen graphischen Darstellungen kann man für $l = 0$, wo l die Kristalllänge bedeutet, auch die Induktionsperiode bestimmen. Es wurde festgestellt, daß bei gleicher Konzentration für verschiedene Deckgläser verschiedene Werte für die Induktionsperiode erhalten werden, da ihre Oberfläche verschieden "aktiv" in der Keimbildung ist. Da Bariumsulfatkristalle unter $c = 5 \cdot 10^{-5}M$ sozusagen kein Wachstum aufweisen, können diese Niederschläge durch Umlösen auch nicht altern.

Dieses wurde experimentell sowohl sedimentometrisch als auch fotografisch nachgewiesen. Kleine Kristalle wurden in Gegenwart von großen Kristallen in einer gesättigten Bariumsulfatlösung 3 Monate bei Zimmertemperatur aufbewahrt, ohne daß sich die kleinen Kristalle lösten.

Dieses zeigt klar, daß bei Sättigungskonzentration die Grenzflächenreaktion wachstumsbestimmend ist.

Die Gegenwart von Fremdionen beeinflußt stark die lineare Wachstumsgeschwindigkeit, wie aus Abb. 4, 5 und 6 hervorgeht, und zwar fällt sie mit wachsender Ionenkonzentration. Gleichzeitig haben erhaltenen Kristalle regelmässigere geometrische Formen.

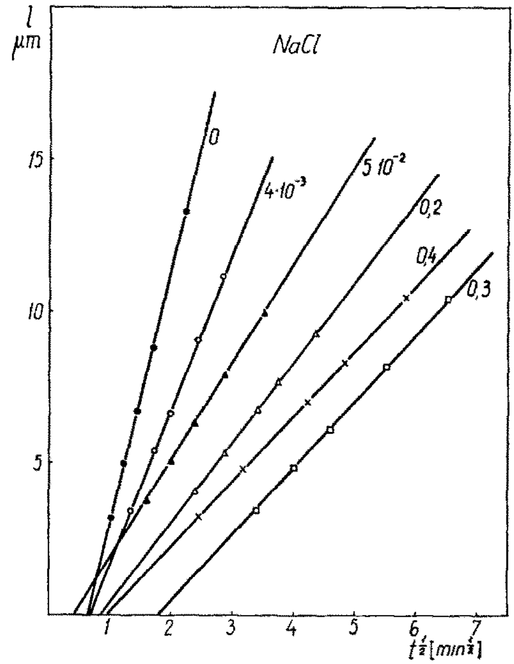


Abb. 4.—Einfluß der Natriumchloridkonzentration auf das Wachstum der Bariumsulfatkristalle; $[BaSO_4] = 5 \cdot 10^{-4}$.

Berechnet man auch in diesen Fällen die Diffusionskoeffizienten bei verschiedenen Konzentrationen, unter Berücksichtigung der Aktivitäten der Barium- und Sulfationen sowie der Löslichkeit des Bariumsulfates in Gegenwart von Fremdionen, so erhält man Werte, die von den Obengenannten wenig abweichen. Das heißt, daß der Wachstumsmechanismus auch in Gegenwart von Fremdionen diffusionsbestimmt ist und daß die Adsorbtion der Ionen die Eingliederung in das Kristallgitter nicht beeinflussen, aber einen Einfluß auf die Kristallform durch die Veränderung der Oberflächenspannung haben.

Wie aus Abb. 7 hervorgeht, hat auch das Verhältnis $[BaCl_2]/[K_2SO_4]$ einen Einfluß auf die Wachstumsgeschwindigkeit.

Grosse Bariumchlorid- und Kaliumsulfatüberschüsse haben einen großen Einluß auf die Kristallform. und zwar führen sie zu dünnen, unregelmässigen Plättchen.

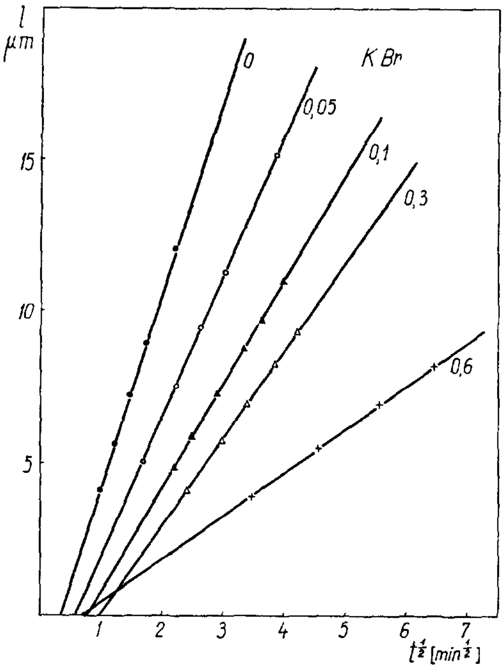


Abb. 5.—Einfluß der Kaliumbromidkonzentration auf das Wachstum der Bariumsulfatkristalle; [$BaSO_4$] = $5 \cdot 10^{-4}$.

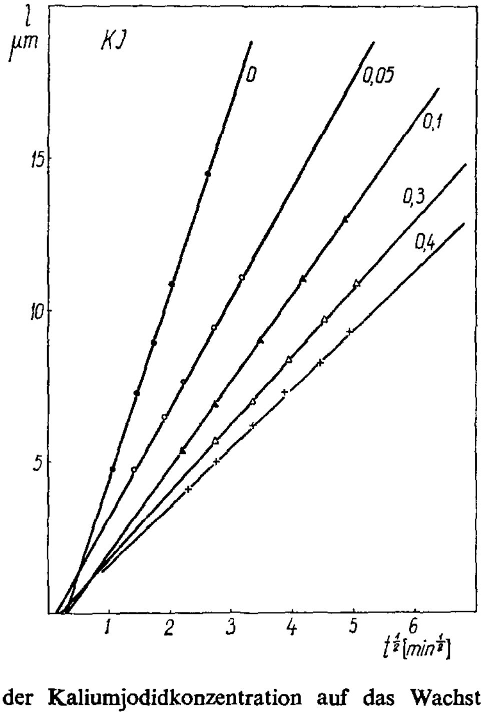


Abb. 6.—Einfluß der Kaliumjodidkonzentration auf das Wachstum der Bariumsulfatkristalle; [$BaSO_4$] = $5 \cdot 10^{-4}$.

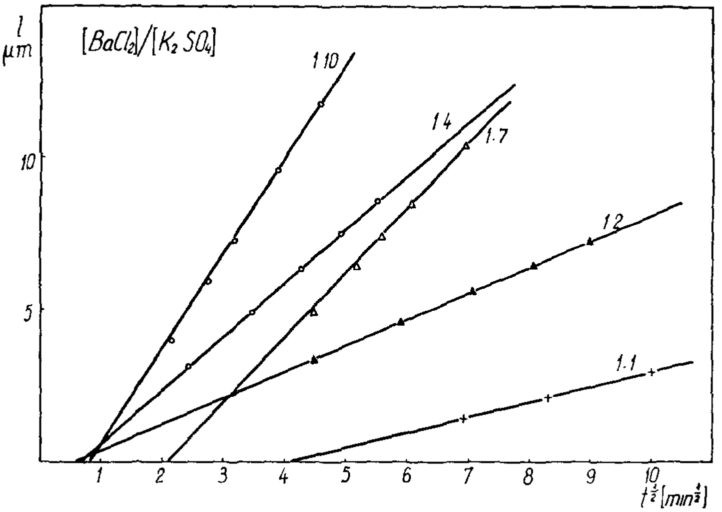


Abb. 7.—Einfluß des Verhältnisses $[BaCl_2]/[K_2SO_4]$ auf das Wachstum der Bariumsulfatkristalle; $[BaSO_4] = 10^{-4}M$.

Diese Methode der Wachstumsbestimmung kann jedoch nur bis zu Konzentrationen von höchstens $1 \cdot 10^{-3}M$ angewendet werden, weil sonst die Kristalle zu nahe aneinander liegen und sich ihre Diffusionshöfe überlappen.

Summary—The influence of foreign ions on the particle size of barium sulphate precipitates has been investigated by sedimentation experiments, establishing that NaCl, $NaNO_3$, KBr, KNO_3 and other salts at high concentrations powerfully hinder the growth of the crystals even at high supersaturation. The linear growth rate has been measured as a function of $BaSO_4$ concentration, foreign ion concentration and $[BaCl_2]/[K_2SO_4]$ ratio. Because the growth is already diffusion controlled at a fivefold supersaturation, the $BaSO_4$ precipitates will not undergo Ostwald ripening. A suitable apparatus has been devised for the investigations.

Résumé—On a étudié l'influence d'ions étrangers sur la dimension de particules de précipités de sulfate de baryum par des expériences de sédimentation, établissant que NaCl, $NaNO_3$, KBr, KNO_3 et d'autres sels à haute concentration gênent puissamment la croissance des cristaux, même à haute sursaturation. On a mesuré la vitesse de croissance linéaire des cristaux en fonction de la concentration en $BaSO_4$, de la concentration en ion étranger et du rapport $[BaCl_2]/[K_2SO_4]$. Etant donné que la croissance est déjà contrôlée par diffusion à une sursaturation de cinq fois, les précipités de $BaSO_4$ ne subiront pas la maturation d'Ostwald. On a conçu un appareil convenable pour les recherches.

LITERATUR

1. C. Liteanu und H. Lingner, *Talanta*, 1970, **17**, 1045.
2. *Idem, ibid.*, 1970, **17**, 1053.
3. V. K. La Mer und R. H. Dinegar, *J. Am. Chem. Soc.*, 1951, **73**, 380.
4. J. R. Campbell und G. H. Nancollas, *J. Phys. Chem.*, 1969, **73**, 1735.
5. R. Marc und W. Wenk, *Z. phys. Chem.*, 1910, **68**, 104.
6. C. W. Davies und G. H. Nancollas, *Trans. Faraday Soc.*, 1955, **51**, 823.
7. G. Kortüm und J. O'M Bockris, *Textbook of Electrochemistry*, Vol. I, S. 192. Elsevier, London, 1951.

8. C. Liteanu und H. Lingner, unveröffentlichte Resultate.
9. K. Neuman, in M. Vollmer, *Kinetik der Phasenbildung*, S. 209. Steinkopff, Dresden, 1939.
10. A. E. Nielsen, *Acta Chem. Scand.*, 1958, **12**, 951.
11. *Idem, ibid.*, 1959, **13**, 784.
12. M. Kahlweit, *Angew. Chem.*, 1965, **77**, 431.

Talanta, 1972, Vol. 19, pp. 953 to 959. Pergamon Press. Printed in Northern Ireland

EFFECT OF SOLVENT EXTRACTION ON THE ATOMIC-ABSORPTION SPECTROPHOTOMETRY IN DETERMINATION OF ppM LEVELS OF CADMIUM WITH DITHIZONE

Y. YAMAMOTO, T. KUMAMARU, Y. HAYASHI and M. KANKE
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda, Hiroshima, Japan

(*Received 9 September* 1971. *Accepted 7 November* 1971)

Summary—Various organic solvents for cadmium dithizonate extraction have been examined for their suitability for subsequent absorption spectrophotometry. The solvents are discussed on the basis of their physical properties. Much enhanced sensitivity is achieved by use of a large aqueous phase/solvent volume ratio. Conditions for the determination of ppM levels of cadmium are described for nitrobenzene and n-butyl acetate as solvents. Dithizone and cadmium dithizonate are very stable in nitrobenzene. The extraction is completely quantitative over the pH range 3·5–10·0. Interference by diverse ions was studied, and their tolerance levels are given.

THE DETERMINATION of traces of several metal ions such as cadmium, lead, copper and zinc, has received increasing attention in connection with water pollution. Atomic-absorption spectrophotometry currently offers the best means for the reliable determination of these metal ions in trace concentrations. However, the determination of parts per milliard (ppM) levels of these elements in water is virtually impossible by direct aspiration of the sample, because the detection limits are usually 0·01 ppm or higher. When these elements exist in waters at concentrations below the detection limits, they can readily be concentrated by solvent extraction, with a consequent increase in sensitivity, caused not only by the favourable phase-volume ratio but also by the effect of the solvent on the atomic-absorption spectrophotometry. The ammonium pyrrolidinedithiocarbamate(APDC)–methyl isobutyl ketone(MIBK) and diethyldithiocarbamate(DDTC)–MIBK systems have been recommended for solvent extraction and atomic-absorption spectrophotometry by several authors,[1-3] because APDC and DDTC give a number of transition element complexes with high extractability over a wide pH range and MIBK has been shown to enhance the atomic absorption considerably. Moreover, the solubility of MIBK in water increases the phase-volume (water:MIBK) ratio[4] further increasing the sensitivity.

It is well known that diphenylthiocarbazone (dithizone) is a strong complexing agent, forming red or orange complexes with a variety of metal ions. Chloroform or carbon tetrachloride have generally been used as the solvents for extraction of dithizonates, but these chlorinated solvents are not suitable in atomic-absorption spectrophotometry because of their incomplete combustion in the flame and the toxity of the decomposition products such as phosgene. Except for the work of Sachdev and West,[5] who used ethyl propionate as solvent, no attempt seems to have been made to utilize metal dithizonate extraction systems for atomic-absorption spectrophotometry(AAS).

In this paper, the utility of various organic solvents for dithizonate extraction and subsequent AAS is studied, using cadmium as a typical element. It appears that the so-called "solvent effect" is primarily related to the aspiration rate which is governed by the physical properties of the solvent. With nitrobenzene and n-butyl acetate, the effect of their partial miscibility with water was investigated by varying the phase-volume ratio.

EXPERIMENTAL

Apparatus

Atomic-absorption measurements were made with a Nippon Jarrell–Ash Model AA-1 EW atomic-absorption spectrophotometer fitted with a Hitachi Model HLA-3 hollow-cathode lamp and equipped with a Yanagimoto Model YR-101 recorder. Radio-activity measurements were made with a Nihonmusen Model R-1360 low-background counter. Viscosity measurements on MIBK were made with an Ubbelohde-type viscometer.

Reagents

All reagents are analytical grade unless otherwise stated and the aqueous solutions are stored in polyethylene bottles. Demineralized water is used.

Cadmium solution, 1000 *ppm*. Dissolve 1·00 g of cadium metal (99·99%) in 10 ml of 3*M* hydrochloric acid and add 2 ml of concentrated sulphuric acid. Evaporate the solution nearly to dryness and ditute to 1000 ml with water.

Cadmium-115*m solution.* Dilute 1 mCi ^{115m}Cd solution (in 0·5*M* hydrochloric acid) to 100 ml with water. This solution contains 20·8 μg of cadmium per ml and is diluted to tracer scale when it is used in the experiment.

Dithizone solutions, 0·03%. Dissolve 75 mg of refined dithizone in 250 ml of a solvent. The solvents used were MIBK, ethyl propionate, n-butyl acetate, nitroethane and nitrobenzene.

Buffer solution, pH 4–6. Prepare acetate buffers by mixing 2*M* acetic acid and 2*M* sodium acetate in suitable ratio.

Procedure

Transfer an aliquot of cadmium solution by pipette into a 50–1000 ml standard flask. Add 5 ml of the buffer solution to adjust the pH of the final solution to 4–6 and dilute to the mark with water. Then transfer the solution into a suitable separatory funnel. Add 10–50 ml of the dithizone solution and shake the funnel for 10 min on a mechanical shaker. Let stand for 15 min, then separate the organic phase. Measure the atomic absorption of cadmium (2288 Å) in the extract against a reference consisting of the solvent saturated with water, under the optimum operating conditions.

RESULTS AND DISCUSSION

Effect of pH and solvent

Effect of pH on the extraction of cadmium dithizonate into various solvents was studied radiochemically with ^{115m}Cd. Five solvents were tested: MIBK, ethyl propionate (EP), n-butyl acetate (BA), nitroethane (NE) and nitrobenzene (NB). Each extraction was done with equal volumes of the two phases, which had previously been mutually saturated. As shown in Fig. 1, all the solvents tested gave complete extraction of cadmium dithizonate over the pH range 3·5–10·0. For practical convenience, pH 5·3 was selected in this experiment.

The effect of the solvent on the atomic absorption of cadmium is shown in Fig. 2. The volume of both phases (which were previously saturated with each other) was 50 ml. In atomic-absorption spectrophotometry the addition of a water-soluble organic solvent in the aqueous phase or use of an extract made with a water-immiscible organic solvent usually affects the sensitivity. This effect may be attributed to two factors: the effect on the aspiration rate, and the effect on atomization efficiency. As shown in Fig. 2, the order of decreasing sensitivity is MIBK $>$ EP $>$ BA $>$ NE $>$ (water) $>$ NB. Table I shows some physical properties of the solvents together with the aspiration rate of the extracts measured here. It is observed that the aspiration rate increases as the viscosity, density and surface tension decrease. It may be said that the sensitivity order is primarily due to the aspiration rate, which is governed by these physical properties. The similar sensitivities of the aqueous solution and NB extract

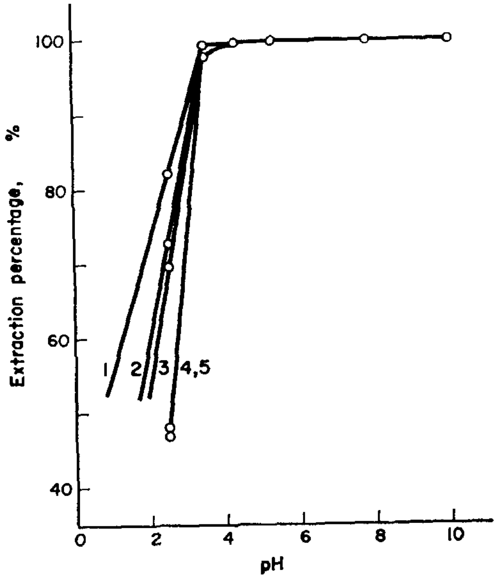


FIG. 1.—Effect of pH on extraction of cadmium dithizonate with various solvents. Aqueous phase 50 ml, organic phase 50 ml. 1—MIBK, 2—NE, 3—NB, 4—EP, 5—BA.

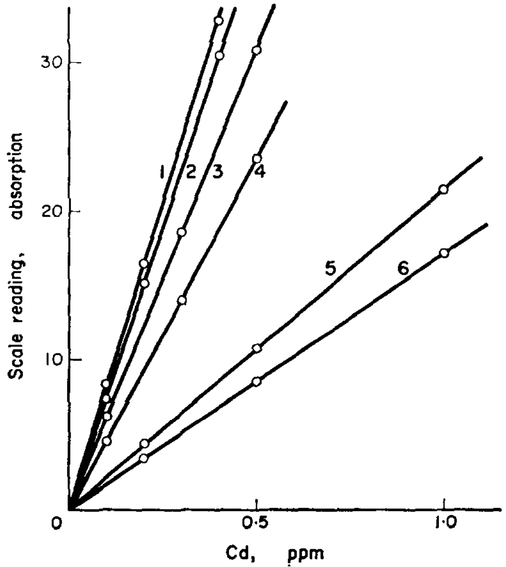


FIG. 2.—Effect of solvent on atomic absorption of cadmium. Aqueous phase 50 ml, organic phase 50 ml. 1—MIBK, 2—EP, 3—BA, 4—NE, 5—water, 6—NB.

TABLE I.—PHYSICAL PROPERTIES OF SOLVENTS[6]

Solvent	Surface tension, *dyne/cm*	Viscosity, *cp*	Aspiration rate *ml/min*	Density, g/cm^3
MIBK	23·64(20°)	0·586(20°)*	10·0*	0·806*
EP	24·27(20°)	0·564(15°)	10·2*	0·893*
BA	25·2 (20°)	0·734(20°)	8·33*	0·881*
NE	31·31(25°)	0·661(25°)	9·22*	1·050*
NB	43·35(20°)	2·165(15°)	4·24*	1·207*
Water	72·75(20°)	1·005(20°)	8·46*	1·000*

* Measured in this experiment.
Temperatures are given in brackets.

suggest that an increased atomization efficiency in the flame with NB compensates the decrease in sensitivity caused by the low aspiration rate of this solvent.

Effect of phase-volume ratio on sensitivity

To obtain higher sensitivity for the determination of ppM levels of cadmium, use of a large initial aqueous phase/solvent volume ratio (V_w/V_o) is required. In subsequent experiments, NB and BA were chosen as typical solvents. The former is a solvent with extremely small solubility in water, and the latter is appreciably soluble. The volume changes of the NB and BA phases after extraction are shown in Fig. 3. The volume after extraction was measured by pipette after centrifugation 15 min after extraction was complete. With increasing V_w/V_o, the volume of the extract with BA appreciably decreases, while that with NB remains almost unchanged. As is shown in Fig. 4, the degree of extraction determined by using cadmium tracer (^{115m}Cd) shows that NB extracts cadmium completely over the whole range of V_w/V_o used, but in the case of BA appreciable loss of the element occurs owing to the partial miscibility of solvent with water. An increasing *relative* absorption with increase in the volume

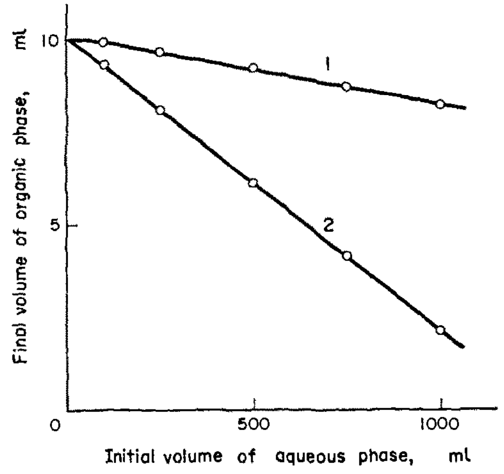


FIG. 3.—Final volume of NB and BA phases after extraction.
Initial volume of organic phase 10 ml.
1—NB, 2—BA.

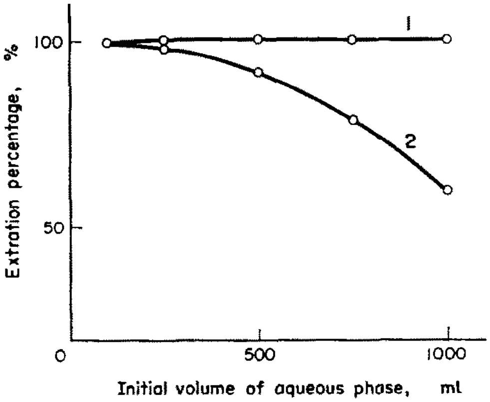


FIG. 4.—Extraction of cadmium dithizonate with NB and BA.
Initial volume of organic phase 10 ml.
1—NB, 2—BA.

ratio (V_w/V_0) is shown in Fig. 5. A much enhanced sensitivity is achieved in BA extraction by use of a larger volume ratio, mainly because of the greater degree of concentraton of the dithizonate in the diminished organic phase. Calibration curves are shown in Fig. 6.

The precision was estimated from 10 samples in each of two series of extractions with $V_w/V_0 = 500/10$. One series (Cd, 20 μg) with NB as solvent gave a standard deviation of 2%, and the other series (Cd 5 μg) with BA gave 5%.

Interferences

Atomic-absorption spectroscopy is relatively free from interferences. However, large amounts of various cations may suppress the extraction of cadmium because of

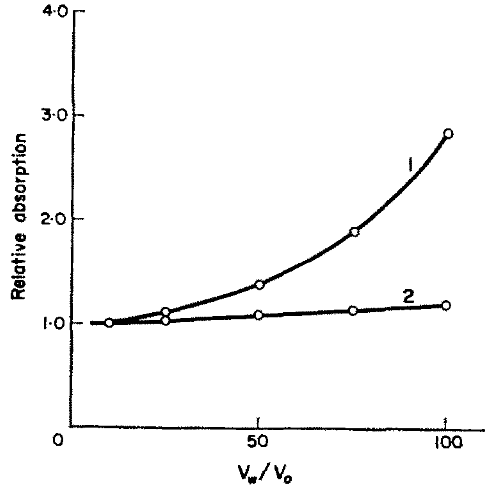


FIG. 5.—Effect of initial volume ratio on atomic absorption of cadmium.
Initial volume of organic phase 10 ml.
1—BA, 2—NB,
Cadmium 5 μg (BA), 20 μg (NB).

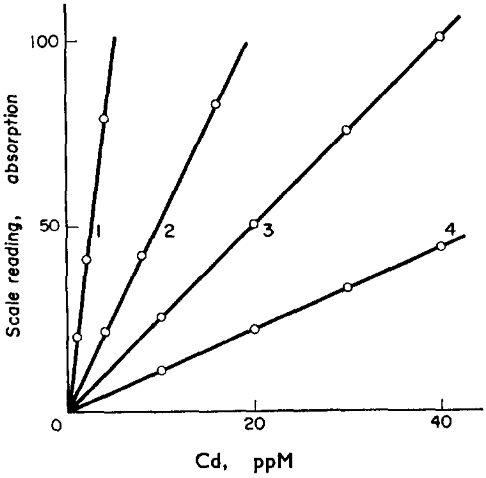


FIG. 6.—Calibration curves for cadmium.
Initial volume of organic phase 10 ml.
Initial volume of aqueous phase:
BA; 1—1000 ml, 2—500 ml;
NB; 3—1000 ml, 4—500 ml.

TABLE II.—Tolerance limits (ppm) for other ions, for error not exceeding 2% in determination of 20 ppM cadmium.

Ion	0·03% Dz	0·15% Dz
Cu(II)	0·5	2·5
Ag(I)	1	~5
Hg(II)	1	~5
Zn	2	10
Pb	2	2·5
Co(II)	50	
Cr(III)	300	
Mn(II)	300	
Fe(III)	300	
Ni(II)	300	
Mg	500	
Ca	500	
Cl^-	500	
NO_3^-	500	
PO_4^{3-}	500	
SO_4^{2-}	500	
$Cr_2O_7^{2-}$	500	
CN^-	300	

their consumption of dithizone. Permissible concentrations causing errors less than 2% in the NB extraction method are shown in Table II.

No interference by alkali and alkaline earth metal ions and by several anions was observed, but large amounts of transition metal ions that react with dithizone markedly lowered the extraction of cadmium. Interference by these ions could be reduced by use of a higher concentration of dithizone.

This extraction system should be suitable for other elements which form stable dithizonates, such as copper, zinc, lead and silver.

Zusammenfassung—Verschiedene organische Lösungsmittel zur Extraktion von Cadmiumdithizonat wurden auf ihre Eignung zur nachfolgenden Absorptions-Spektrophotometrie geprüft. Die Lösungsmittel werden an Hand ihrer physikalischen Eigenschaften diskutiert. Stark verbesserte Empfindlichkeit erhält man durch Anwendung eines großen Volumenverhältnisses von wäßriger Phase zu Lösungsmittel. Die Arbeitsbedingungen zur Bestimmung von ppM-Mengen Cadmium werden mit Nitrobenzol und n-Butylacetat als Lösungsmittel angegeben. Dithizon und Cadmiumdithizonat sind in Nitrobenzol sehr stabil. Die Extraktion ist im pH-Bereich 3,5–10,0 vollständig quantitativ. Die Störung durch verschiedene Ionen wurde untersucht und die Toleranzmengen werden angegeben.

Résumé—On a examiné divers solvants organiques pour l'extraction du dithizonate de cadmium quant à leur convenance pour la spectrophotométrie d'absorption subséquente. On discute des solvants sur la base de leurs propriétés physiques. On obtient une sensibilité de beaucoup accrue par l'emploi d'un grand rapport de volume phase aqueuse/solvant. On décrit les conditions de dosage du cadmium à l'échelle du ppM avec le nitrobenzène et l'acétate de *n*-butyle comme solvants. La dithizone et le dithizonate de cadmium sont très stables en nitrobenzène. L'extraction est totalement quantitative dans le domaine de pH 3,5–10,0. On a étudié la gêne apportée par divers ions, et l'on donne leurs niveaux de tolérance.

REFERENCES

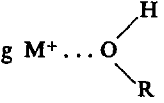
1. J. E. Allan, *Spectrochim. Acta*, 1961, **17**, 467.
2. T. Takeuchi, M. Suzuki and M. Yanagisawa, *Anal. Chim. Acta*, 1966, **36**, 258.
3. J. A. Platte, *Trace Inorganics in Water*, in *Advances in Chemistry Series*, Vol. 73, p. 247 American Chemical Society Publications, 1967.
4. Y. Yamamoto, T. Kumamaru, Y. Hayashi and M. Kanke, *J. Hyg. Chem. (Japan)*, 1971, **17**, 119.
5. S. L. Sachdey and P. W. West, *Anal. Chim. Acta*, 1969, **44**, 301.
6. A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr., *Organic Solvents*, in *Technique of Organic Chemistry*, Vol. VII, Interscience, New York, 1955.

Talanta, 1972, Vol. 19, pp. 961 to 969. Pergamon Press. Printed in Northern Ireland

UNIVALENT CATION-EXCHANGE IN ORGANIC SOLVENT WATER AND ORGANIC SOLVENT–WATER–PHENOL MIXTURES

J. G. JONES and J. D. R. THOMAS
Department of Chemistry, University of Wales Institute of Science and Technology, Cardiff, Wales

(*Received* 4 *August* 1971. *Accepted* 12 *November* 1971)

Summary—Selectivity coefficients, K_H^M, for the exchange of alkali metal ions and ammonium ions with the hydrogen form of ZeoKarb 225 cation-exchange resin have been determined in various organic solvent–water and organic solvent–water–phenol mixtures. There is an increase in K_H^M in passing from purely aqueous conditions to media of increasing organic solvent content, frequently with the effect of producing magnified differences and selectivity reversals between one ion and another. The results are discussed in terms of the relationship between K_H^M and the reciprocal of the dielectric constant of the medium and also in the light of free energies of transfer of cations between methanol–water systems. The effect of phenol giving a lowering of K_H^{Cs} in methanol–water, of K_H^K and K_H^{Na} in ethanol–water and of K_H^{Na} and K_H^{Li} in acetone–water systems cannot be fully reconciled with the mechanism involving  $M^+ \ldots O\begin{smallmatrix}H\\R\end{smallmatrix}$ bonding proposed by earlier workers.

USEFUL information is available on cation-exchange processes in non-aqueous and mixed solvent systems.[1] The frequent increase in selectivity coefficients for the exchange of given pairs of ions as the dielectric constant of the solvent medium decreases is interesting, and the linear relation between log selectivity coefficient and the reciprocal of the dielectric constant of the medium[2-11] has initiated several explanations. These range from the hypothetical desolvation energy involved in ion-exchange[4,5] to ion-pair formation[7,8] and to changes in the solution and resin-phase activity coefficients.[9,10] Variations in trends can lead to changes of order in selectivities, for example, on Dowex 50 × 8 the aqueous selectivity order of $Cs^+ > K^+ > CH_3NH_3^+ > NH_4^+ > Na^+ > Li^+$ is twice reversed in methanol, where $K^+ > Cs^+$ and $Na^+ > CH_3NH_3^+ > NH_4^+$.[9]

This paper extends existing knowledge[9] for univalent cation exchange in methanol–water and ethanol–water to a larger range of univalent cations and to acetone–water systems. Additionally, phenol was incorporated in the media in order to supplement available information on the greater selectivity of bifunctional sulphonated phenol-formaldehyde exchangers for the heavier alkali metal ions, compared with sulphonated polystyrene–divinyl benzene exchangers,[11,12,13] and also to gain further knowledge of the lowering of the affinity of monofunctional sulphonic acid resins for Cs^+ ions when the solvent medium contains phenol.[11]

EXPERIMENTAL

Materials

Solvents. Analytical-reagent grade methanol and acetone. BPC grade absolute ethanol.

Salts. Analytical-reagent grade chlorides of sodium, potassium, caesium and ammonium, and Koch-Light (purity > 99·9%) rubidium chloride. Lithium chloride was prepared from analytical-reagent grade lithium carbonate assayed acidimetrically.

Phenol. Analytical-reagent grade.

Ion-exchange resin. ZeoKarb 225 resin (8% DVB; 52–100 mesh) supplied in the sodium form was converted into the hydrogen form by a column technique using five bed-volumes of 10% hydrochloric acid. The resin was washed free from acid with demineralized water and then repeatedly washed with the solvent (for example, with methanol for studies involving methanol) until the refractive index of the eluate was that of the pure solvent. To avoid possible adverse thermal effects, the resin was dried for 24 hr at 30°.

In order to equate more precisely the results from different resin batches, the loss of weight on drying at 105° was determined for each batch before use. The exchange capacity of the hydrogen-form resin was determined by conversion into the sodium form and estimation of the displaced hydrogen ions by potentiometric titration to pH 7·0 with standard sodium hydroxide.

Equilibration procedure

Equilibrium studies were made with glass-stoppered Quickfit tubes (54 ml capacity) containing ion-exchange resin and liquid phase of initial concentration 0·1*M* with respect to the cation. To prepare the mixture for equilibration, 1·00(±0·01) g of air-dried resin was weighed into the tube, and in the case of systems involving phenol, 2·50(±0·01) g phenol were added. According to the liquid phase composition required, 0·0, 5·0, 15·0, 25·0, 35·0 or 45·0 ml of pure solvent were measured into the tubes and demineralized water was added to give a total volume of 45·0 ml. The cation was then added as 5·0 ml of 1·0*M* alkali metal/ammonium chloride, thus making the initial composition of the liquid phase of each series of six tubes 0, 10, 30, 50, 70 and 90% organic solvent, respectively.

The exchange equilibria were allowed to establish at 30 ± 1° in an air thermostat by allowing the resin to cascade through the solution. This was achieved by placing the tubes containing the resin-solvent system on a rotating wheel within the thermostat. The run was allowed to proceed for 16 hr, although preliminary experiments showed that equilibrium was reached in 4 hr and that runs of 24 hr did not alter the equilibrium.

Analysis of equilibrium solutions

After equilibration the resin and liquid phase were separated by transfer of the liquid to a Buchner flask under gentle suction through a sintered-glass disc interposed between two Quickfit cones connecting the Buchner flask and equilibration tube. A 25-ml portion of the liquid phase was titrated potentiometrically with 0·1*M* sodium hydroxide to pH 7·00, a glass and calomel electrode pair being used. The titre corresponds to the hydrogen ions liberated from the resin during equilibration; it also corresponds to the metal/ammonium ion associated with the resin phase at equilibrium. The selectivity coefficients, $K_H{}^M$, for the resin phase were calculated by computer, using a Fortran program.

In the case of systems involving potassium, rubidium and caesium, a check was made on the total cation content of the liquid phase by determining its metal ion concentration gravimetrically as the tetraphenylborate salt. Table I is representative of the results obtained and confirms that the hydrogen ion content of the liquid phase corresponds to the metal/ammonium ion content of the resin phase.

TABLE I.—RESULTS OF THE GRAVIMETRIC DETERMINATION OF RUBIDIUM IN THE EQUILIBRIUM LIQUID PHASE FOR THE METHANOL-WATER SYSTEM

Total rubidium added = 427·4 mg

Methanol, %	Rb^+ in liquid phase (determined gravimetrically), *mg*	Rb^+ in resin phase (calculated from H^+ ion content of liquid phase) *mg*	Total Rb^+ *mg*
0	205·1	222·3	427·4
10	188·6	237·6	426·2
30	168·0	259·9	427·9
50	147·6	278·7	426·3
70	120·3	306·0	426·3
90	104·7	318·0	422·7

RESULTS

Figure 1 gives plots of log selectivity coefficients (log $K_H{}^M$) *vs.* volume fraction of water for the univalent cation exchanges in the various organic solvent–water and organic solvent–water–phenol mixtures. Difficulties were encountered with solubility problems for acetone–water systems with a high content of acetone, for potassium, rubidium, caesium and ammonium chlorides, and the results for these show trends different from those that might otherwise have been obtained.

The order of resin affinities for cations in the various systems studied is given in Tables II, III and VI, while Table IV and V show the enhancement and alterations in $K_H{}^M$ between water and organic solvent–water (0·1 volume fraction water) mixtures in the absence (Table IV) and in the presence (Table V) of phenol.

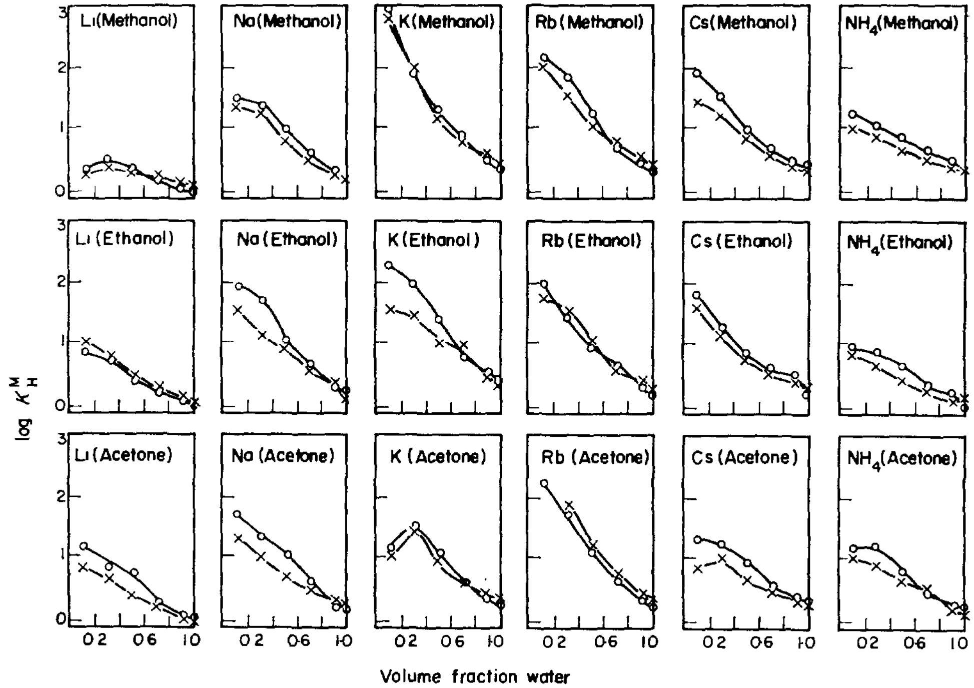


FIG. 1.—Selectivity coefficients of alkali metal ions and ammonium ions between ZeoKarb 225 and various organic solvent–water (○) and organic solvent–water–phenol mixtures (×).

DISCUSSION

Organic solvent–water systems

The results for methanol–water media in the absence of phenol are in broad agreement with those of Fessler and Strobel[9] except that the selectivity maxima noted by them and other workers[6,14] using resins other than ZeoKarb 225, were not so much in evidence. However, because of solubility considerations, the present studies were not extended to media containing less than 0·1 volume fraction water. Nevertheless, the maximum noted by Fessler and Strobel[9] for potassium in methanol–water (at 0·2 mole fraction water in methanol) should have been evident. Instead, the selectivity coefficient for potassium rises steadily to a phenomenally high level of 978 at 0·1 volume fraction (0·19 mole fraction) water in methanol compared with just 2·34 in water. In this respect it is perhaps significant that log $K_H{}^M$ is a linear function of $1/D$ (Fig. 2) where D is the macroscopic dielectric constant of the external solution, as used by Fessler and Strobel.[9] Indeed, while Fessler and Strobel confirm the linear relation

TABLE II.—ORDER OF AFFINITY OF ZEOKARB 225 (H FORM) FOR ALKALI METAL/AMMONIUM IONS IN VARIOUS ORGANIC SOLVENT-WATER MEDIA AT 30°C

Solvent composition % Organic solvent	Affinity (decreasing) →					
Methanol						
0	K	Cs	Rb	NH$_4$	Na	Li
10	K	Cs	= NH$_4$	Rb	Na	Li
30	K	Rb	Cs	= NH$_4$	Na	Li
50	K	Rb	Na	Cs	NH$_4$	Li
70	K	= Rb	Cs	Na	NH$_4$	Li
90	K	Rb	Cs	Na	NH$_4$	Li
Ethanol						
0	K	Cs	Rb	Na	NH$_4$	Li
10	K	Cs	Rb	Na	NH$_4$	Li
30	K	Na	Rb	Cs	NH$_4$	Li
50	K	Na	Rb	Cs	NH$_4$	Li
70	K	Na	Rb	Cs	NH$_4$	Li
90	K	Rb	Na	Cs	NH$_4$	Li
Acetone						
0	Cs	Rb	= K	= NH$_4$	Na	Li
10	Cs	= Rb	= K	NH$_4$	Na	Li
30	Rb	K	Cs	Na	NH$_4$	Li
50	Rb	K	= Na	Cs	NH$_4$	Li
70	Rb	K	Na	Cs	NH$_4$	Li
90	Rb	Na	Cs	NH$_4$	K	= Li

TABLE III.—ORDER OF AFFINITY OF ZEOKARB 225 (H FORM) FOR ALKALI METAL/AMMONIUM IONS IN VARIOUS ORGANIC SOLVENT–WATER–PHENOL MEDIA AT 30°C

Phenol content 5% in each case

Solvent composition % Organic solvent	Affinity (decreasing) →					
Methanol						
0	K	Rb	Cs	NH$_4$	Na	Li
10	K	Cs	Rb	NH$_4$	Na	Li
30	K	Rb	Cs	Na	NH$_4$	Li
50	K	Rb	Cs	Na	NH$_4$	Li
70	K	Rb	Na	Cs	NH$_4$	Li
90	K	Rb	Cs	Na	NH$_4$	Li
Ethanol						
0	K	Cs	Rb	NH$_4$	Na	Li
10	K	Cs	Rb	Na	Li	NH$_4$
30	K	Rb	Na	Cs	Li	NH$_4$
50	Rb	K	Na	Cs	Li	NH$_4$
70	Rb	K	Cs	Na	Li	NH$_4$
90	Rb	Cs	Na	K	Li	NH$_4$
Acetone						
0	K	Cs	Rb	Na	= NH$_4$	Li
10	K	Rb	Cs	Na	NH$_4$	Li
30	Rb	K	NH$_4$	Cs	Na	Li
50	Rb	K	Na	Cs	NH$_4$	Li
70	Rb	K	Cs	Na	NH$_4$	Li
90	Na	K	NH$_4$	Cs	Li	

TABLE IV.—SELECTIVITY COEFFICIENTS, K_H^M, IN WATER AND ORGANIC SOLVENT–WATER AT 30°C

Volume fraction water	Organic solvent	K_H^M					
		Li–H	Na–H	K—H	Rb–H	Cs–H	NH_4–H
1·0*	Methanol	0·92	1·61	2·34	2·12	2·29	1·86
	Ethanol	0·83	1·62	2·29	1·64	1·71	1·13
	Acetone	1·03	1·50	1·89	1·89	2·06	1·89
0·1	Methanol	2·08	33·5	978	147	79	15·6
	Ethanol	7·5	83	183	99	67	8·5
	Acetone	15·2	53	15·2†	173	21·4†	16·3†

* Three sets of figures arise for water because the preliminary resin treatment involves washing with organic solvent.

† These figures may be low because of poor solubility.

TABLE V.—SELECTIVITY COEFFICIENTS, K_H^M, IN WATER AND ORGANIC SOLVENT–PHENOL–WATER AT 30°C

Phenol content 5% in each case

Volume fraction water	Organic solvent	K_H^M					
		Li–H	Na–H	K–H	Rb–H	Cs–H	NH_4–H
1·0*	Methanol	1·23	1·58	2·57	2·29	2·20	1·88
	Ethanol	0·61	1·22	2·21	1·70	1·85	1·34
	Acetone	0·89	1·60	2·37	2·06	2·22	1·62
0·1	Methanol	1·95	21·3	611	106	27·2	9·9
	Ethanol	10·5	38	34·5	55	40	6·7
	Acetone	7·3	21·8	11·2†	—	7·6†	12·3†

* Three sets of figures arise for water because the preliminary resin treatment involves washing with organic solvent.

† These figures may be low because of poor solubility.

between log K_H^M and $1/D$ for water-rich methanol noted by other workers[5,15,16,17] they stress the shortness of the linear region, in general from 0·7 or 0·8 to 1·0 mole fraction (0·5 or 0·6–1·0 volume fraction) water. In this work, the linear range is often longer and particularly so for potassium (Fig. 2).

The tendency for selectivity maxima clearly leads to a breakdown of the linear relation between log K_H^M and $1/D$ (Figs. 1 and 2), and while the interpretation of Fessler and Strobel,[9] based on the effect of the medium on ionic activity coefficients, may be valid, other considerations may hold. These may include the inability of large solvated ions, such as those of lithium and sodium, to penetrate the shrunken resin and hence upset activity and energy considerations.

The methanol–water trends are also evident for the ethanol–water systems, but the tendency for K_H^M to maximize is not so evident and neither does potassium show such a phenomenal increase of affinity for the resin with diminishing water content of the medium. This may be due to the more shrunken state of the resin in media of lower dielectric constant. In this respect, it may be relevant that sodium and lithium now show an enhancement of selectivity for the resin (Fig. 1) which might be attributed to the hydration shell being phased out, thus permitting penetration of even the smaller pores of the resin in ethanol media. Indeed, the pattern for sodium and lithium is

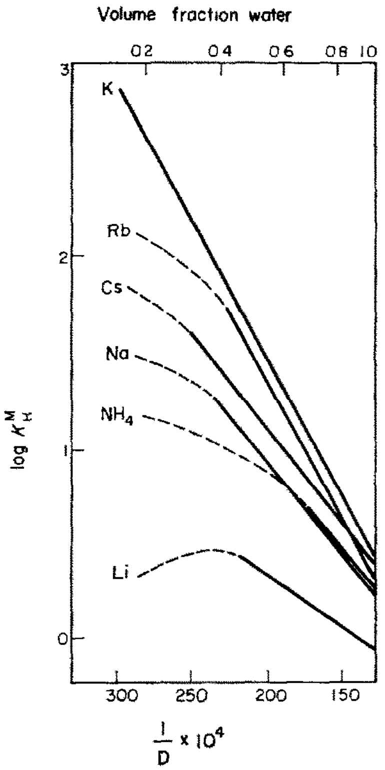


FIG. 2.—Plot of log selectivity coefficient *vs.* reciprocal of the dielectric constant (D) for methanol-water system.

similar in acetone–water media. In these latter media, however, maxima become prominent for potassium, caesium and ammonium ions, but this may be due to the poor solubility of the salts used in acetone-rich media and the affinity for the resin (due to its shrunken state) may be inadequate to overcome this. Poor solubility is, however, not very plausible as an explanation (the solid salt noted on first making up the batch disappears during equilibration), for gravimetric studies on the equilibrium liquid phase together with its hydrogen ion content gave a full mass-balance for the cation.

The phenomenal increase in K_H^M, in passing from purely aqueous conditions to media of increasing organic solvent content. (Fig. 1), frequently with the effect of producing magnified differences between one ion and another, is remarkable and merits consideration in the light of standard molar free energies of transfer for single cations between various media.[18] Such free energies of transfer between water and water–methanol media are shown in Table VI, from which it can be seen that the cations are in an increasingly lower free-energy state with increasing methanol content of the medium.

The relevance of the values is to be seen in the context of the observation of Davies and Thomas[19] in that the medium associated with the resin phase is predominantly aqueous. Thus, the fact that the alkali metal ions, Li^+, Na^+ and K^+ are sequentially in a higher (more positive) free energy state than hydrogen (Table VI)

TABLE VI.—STANDARD FREE ENERGY OF TRANSFER (*J/mole*) AT 25°C OF SINGLE CATIONS FROM WATER TO WATER–METHANOL MEDIA[18]

Ion	Water–10% w/v methanol	Water–43·12% w/v methanol
H^+	±2060	±11760
Li^+	±1390	±8400
Na^+	−920	±5900
K^+	−800	±5000
	(±250 J/mole)	(±2500 J/mole)

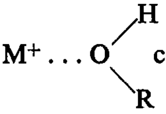
suggests that hydrogen ions prefer the more organic liquid medium, thus leading to an increase in $K_H{}^M$ as the organic solvent content of the medium is increased and to increasingly higher values of $K_H{}^M$ in the series Li^+, Na^+, K^+ as the free energy of the ion relative to hydrogen becomes more positive. In this last respect, it would be interesting to learn how free energy transfer data for rubidium and caesium fit into the ion-exchange pattern.

No amount of theoretical explanation will alter the feature of potential analytical interest and that is the extent to which mixed organic solvent–water media are capable of creating large differences in selectivity coefficients (Table IV). The several selectivity order reversals noted in these systems (Table II) offer a basis for variety in separation schemes. Fessler and Strobel[9] have already remarked on this feature and the present results are also consistent with those of Gorshkov, Korolev and Shabanov[11] who found that the effect of added methanol on $K_H{}^M$ for alkali metal cations increases on going from Li^+ to K^+ and decreases on going from K^+ to Cs^+. This study was confined to methanol–water media of more than 0·4 mole fraction (0·23 volume fraction) water and therefore does not extend so much into the region where maxima in selectivity coefficient data might be observed.

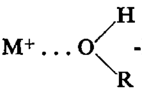
Organic solvent–phenol–water systems

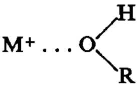
An important objective of the study by Gorshkov, Korolev and Shabanov[11] was the effect of 57·5–72% phenol on selectivity, for the monofunctional sulphonic acid cation-exchangers KU-1 and Dowex 50 × 2. It was found that phenol appreciably lowers $K_H{}^M$, particularly for the caesium exchange. Hence it is interesting to note that the milder conditions of the present investigation (using 5% phenol) sufficiently lower $K_H{}^{Cs}$ to cause a pronounced difference between it and the greater $K_H{}^{Rb}$ (Fig. 1 and Tables IV and V).

Added phenol gives different patterns for the ethanol and acetone systems (Fig. 1) in that the more pronounced lowering of $K_H{}^M$ at high organic solvent content occurs for sodium and potassium in the ethanol systems and for lithium, sodium and caesium in the acetone systems. However, $K_H^{NH_4}$ is almost always lower in the presence of phenol for all three systems studied.

The interesting aspect of the trend in $K_H{}^M$ lowering is that, with the exception of caesium in acetone, the trend is towards the lower atomic number alkali metal ions as the dielectric constant of the organic solvent decreases ($D = 80, 33, 25, 21$ for water, methanol, ethanol, acetone respectively). Such a trend is not consistent with an explanation[11] which rules out ion-dipole interactions. Such interactions should weaken as the ionic radius increases and as the dipole moment falls (that is, on going from Rb^+ to Cs^+ and also from water to methanol to ethanol to acetone and to phenol). However, because of the lowering of K_H^{Cs} in methanol–water media containing phenol, Gorshkov, Korolev and Shabanov[11] proposed the mechanism of Esafov[20] involving an  $M^{+}\ldots O{<}^{H}_{R}$ complex where the metal–oxygen bond will be stronger, the weaker the hydration of the cations, and the more complex the hydrocarbon radical of R in ROH, that is, it will be stronger for Cs^+ than Rb^+ and stronger for phenol than methanol.

The present results suggest that ion-dipole interaction cannot be entirely ruled out, for, as noted above, the K_H^M lowering associated with phenol moves towards the lighter alkali metal ions. This is consistent with the ions becoming less hydrated as the dielectric constant of the organic solvent decreases, while the anomalous position of caesium in acetone arises from solubility considerations. The real explanation is clearly complex, demanding further study, and must await the results of a continuing programme. For example, acidity considerations may have their part to play, for both alcohols and phenols have different acidity effects from water.[18,21]

Zusammenfassung—In verschiedenen Gemischen aus organischem Lösungsmittel und Wasser oder organischem Lösungsmittel, Wasser und Phenol wurden die Selektivitätskoeffizienten K_H^M für den Austausch von Alkalimetall- und Ammoniumionen mit der protonierten Form des Kationenaustauschharzes ZeoKarb 225 bestimmt. K_H^M steigt an, wenn man von rein wäßriger Lösung zu Medien mit steigendem Gehalt an organischem Lösungsmittel übergeht; oft sind damit größere Differenzen und Umkehrungen der Selektivität zwischen zwei Ionen verbunden. Die Ergebnisse werden im Hinblick auf die Beziehung zwischen K_H^M und der reziproken Dielektrizitätskonstanten des Mediums sowie auf die freien Überführungsenergien von Kationen zwischen Methanol-Wasser-Systemen diskutiert. Der Einfluß von Phenol, das K_H^{Cs} in Methanol-Wasser, K_H^K und K_H^{Na} in Äthanol-Wasser sowie K_H^{Na} und K_H^{Li} in Aceton-Wasser erniedrigt, kann mit dem von früheren Autoren vorgeschlagenen Mechanismus, der eine  $M^{+}\ldots O{<}^{H}_{R}$ -Bindung enthält, nicht voll in Einklang gebracht werden.

Résumé—On a déterminé les coefficients de sélectivité K_H^M pour l'échange d'ions metalliques alcalins et d'ions ammonium avec la forme hydrogène de la résine échangeuse de cations ZeoKarb 225 dans divers mélanges solvant organique-eau et solvant organique-eau-phénol. Il y a un accroissement de K_H^M lorsqu'on passe de conditions purement aqueuses à des milieux à teneur croissante en solvant organique, avec fréquemment pour effet la production de différences amplifiées et d'inversions de sélectivité entre ions. On discute des résultats en fonction de la relation entre K_H^M et l'inverse de la constante diélectrique du milieu et aussi à la lumière des énergies libres de transfert de cations entre les systèmes méthanol-eau. L'influence du phénol donnant un abaissement de K_H^{Cs} en méthanol-eau, de K_H^K et de K_H^{Na} en systèmes ethanol-eau et de K_H^{Na} et K_H^{Li} en systèmes acétone-eau ne peut être pleinement conciliée avec le mécanisme mettant en jeu la liaison  $M^{+}\ldots O{<}^{H}_{R}$ proposé par des auteurs antérieurs.

REFERENCES

1. G. J. Moody and J. D. R. Thomas, *Analyst*, 1968, **93**, 557.
2. A. R. Gupta, *J. Phys. Chem.*, 1965, **69**, 341.
3. M. R. Ghate, A. R. Gupta and J. Shankar, *Indian J. Chem.*, 1965, **3**, 287.
4. T. Sakaki and H. Kakihana, *Bull. Chem. Soc. Japan*, 1955, **28**, 217.
5. T. Sakaki, *ibid.*, 1955, **28**, 220.
6. T. Sakaki and H. Kakihana, *Kagaku* (*Tokyo*) 1953, **23**, 471.
7. H. P. Gregor, D. Nobel and M. H. Gottlieb, *J. Phys. Chem.*, 1955, **59**, 10.
8. V. T. Athavale, C. V. Krishnan and Ch. Venkateswarlu, *Inorg. Chem.*, 1964, **3**, 533.
9. R. G. Fessler and H. A. Strobel, *J. Phys. Chem.*, 1963, **67**, 2562.
10. I. T. Owia, *Sci. Repts. Tohoku Univ.*, 1957, **41**, 129.
11. V. I. Gorshkov, Y. Z. Korolev and A. A. Shabanov, *Zh. Fiz. Khim.*, 1966, **40**, 1878.
12. F. Nelson, D. C. Nichelson, H. O. Phillips and K. A. Kraus, *J. Chromatog.*, 1965, **20**, 107.
13. T. Nozaki and K. Manabe, *Bunseki Kagaku*, 1960, **9**, 316.
14. R. W. Gable and H. A. Strobel, *J. Phys. Chem.*, 1956, **60**, 513.
15. G. M. Panchenkov, V. I. Gorshkov and M. V. Kuklanova, *Zh. Fiz. Khim.*, 1958, **32**, 361, 616.
16. A. T. Davydov and R. F. Skolbionok, *ibid.*, 1958, **32**, 1703.
17. H. Kakihana and K. Sekiguchi, *Nippon Yokugaku Zasshi*, 1955, **75**, 111.
18. D. Feakins and P. Watson, *Chem. Ind. London*, 1962, 2008.
19. C. W. Davies and J. J. Thomas, *J. Chem. Soc.*, 1952, 1607.
20. V. I. Esafov, *Zh. Obshch. Khim.*, 1958, **28**, 1212.
21. J. Hine, *Physical Organic Chemistry*, p. 80. McGraw-Hill, London, 1956.

Talanta, 1972, Vol. 19, pp. 971 to 974. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Studies on the polymer + plasticizer membrane-electrode—VIII* Use of the PVC + tricresyl phosphate membrane as indicating electrode in potentiometric precipitation titration

(*Received* 17 *June* 1971. *Accepted* 27 *November* 1971)

THE MEMBRANE-ELECTRODE obtained[1] by plasticizing PVC with tricresyl phosphate has been successfully used in potentiometric titration of strong acids and bases,[2,3] weak acids and bases,[4] salts that give alkaline hydrolysis,[5] mixtures of acids and bases,[4] organic acids and bases,[6] and in automatic acid–base potentiometric titrations.[7] The membrane-electrode is sensitive to certain cations such as Ag^+, Tl^+, Hg_2^{2+}, Na^+ and K^+.[8] This permits the electrode to be used as transducer in potentiometric titration of certain halides and pseudohalides, if solutions of these cations are used as titrants.

EXPERIMENTAL

The electrolytic cell used is represented by:

SCE | satd. KNO_3 | internal soln. | membrane | external soln. | satd. KNO_3 | SCE

A saturated potassium nitrate bridge was used in order to avoid contact of the calomel electrodes with the Ag^+, Tl^+, or Hg_2^{2+} solutions. Measurements were made at room temperature while the solution was being stirred.

To show the sensitivity of the membrane-electrode to Ag^+, Tl^+ and Hg_2^{2+} the electrode functions are given in Fig. 1. It is obvious that when these cations are used as titrants, the membrane-electrode potential will change very sharply simultaneously with the appearance of an excess of the titrant.

Titration of halides and pseudohalides with $AgNO_3$

Titration curves for halides and pseudohalides (50-ml 0·02*M* samples, 0·1*M* silver nitrate) have the typical *S*-shape of potentiometric titration curves, and the potential break is about 100 mV. The equivalence volumes, calculated according to the Hahn-Weiler method,[9] have been compared with those obtained by use of indicators (chromate for chloride, eosin for bromide and iodide, and ferric alum for thiocyanate), in order to characterize the accuracy of the titrations. The results are given in Table I.

TABLE I.—ACCURACY AND PRECISION OF HALIDE AND PSEUDOHALIDE TITRATIONS WITH SILVER NITRATE

Anion	ΔE*, *mV*	$V_{H\text{-}W}$,† *ml*	V_{ind},‡ *ml*	Error, %
Cl^-	75	7·63	7·65	−0·3
Br^-	115	8·37	8·40	0·4
I^-	125	9·87	9·85	−0.2
SCN^-	90	8·63	8·60	0·4

* For titrant interval from $V_e - 1\%$ to $V_e + 1\%$, where V_e is the equivalence-point volume.
† Equivalence-point volume calculated by the Hahn–Weiler method.
‡ Volume of titration with indicator end-point.

When 0·02*M* potassium iodide is titrated with 0·1*M* silver nitrate at different pH values the potential break decreases with increasing acidity, being 120 mV at pH 4, 105 mV at pH 3, 80 mV at pH 2 and 40 mV at pH 1. In fact, under the conditions used, H^+ and Ag^+ ions are competitive in determining the membrane potential, especially after the equivalence point. The potentials of the initial

---

* Part VII, *Rev. Roumanie Chim.*, 1971, **16**, 559.

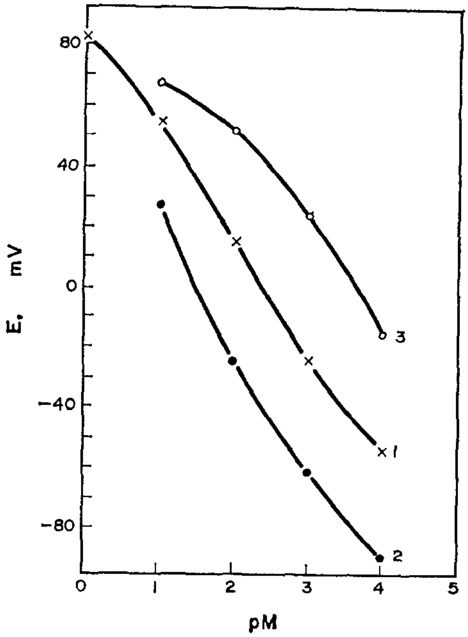


FIG. 1.—pM electrode functions.
1—Ag^+; *2*—Tl^+; *3*—Hg_2^{2+}.

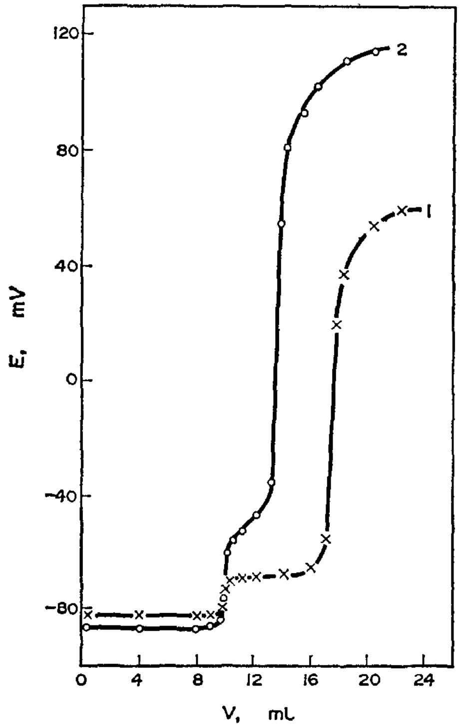


FIG. 2.—Titration of $Cl^- + I^-$ mixture with $0{\cdot}1M$ $AgNO_3$.
1—$0{\cdot}02M$ KI + $0{\cdot}02M$ KCl
2—$0{\cdot}02M$ KI + $0{\cdot}01M$ KCl

solutions are different because of the different acidities used, since the concentration of iodide is the same in all.

The influence of the concentrations of the titrand and titrant has been studied for the iodide-silver titration. The potential break is 100–120 mV for iodide in the range 0·001–0·1M titrated with silver solution ten times as concentrated. The equivalence point can still be easily located even if $10^{-4}M$ iodide is titrated with $10^{-3}M$ silver (60-mV break).

Titration of halide mixtures is satisfactory for $Cl^- + I^-$ but not for $Cl^- + Br^-$ or $Br^- + I^-$. For $Cl^- + I^-$ mixtures the first equivalence point corresponds to the iodide. The potential break is a function of the chloride concentration. The lower the concentration of chloride the larger the potential jump at the first equivalence point (Fig. 2).

Determination of halides with Tl^+ *and* Hg_2^{2+}

Thallous acetate is suitable as titrant for iodide but not for bromide and chloride, the solubility of thallium bromide and chloride being too high to ensure the accuracy needed for the potentiometric titration. The potential break for iodide is only 20–40 mV.

Titration of chloride with mercurous nitrate is similar to that for chloride with thallous acetate, the potential jump being much smaller (10–15 mV) than that obtained in titration with silver nitrate.

Automatic potentiometric titration of iodide

The fast response of the membrane-electrode permits its use in automatic potentiometric determinations. The speed of response was determined by automatically recording the potential of the electrode (on a Radelkis OH 102 polarograph) when it was suddenly introduced into the solution studied: 0·1M silver nitrate, 0·01M thallous acetate or 0·01M mercurous nitrate (Fig. 3). The membrane-electrode shows a practically constant potential in about 4 sec. On the basis of this fast response, the membrane-electrode was used in automatic titration of iodide with silver nitrate, by either direct or derivative potentiometry.

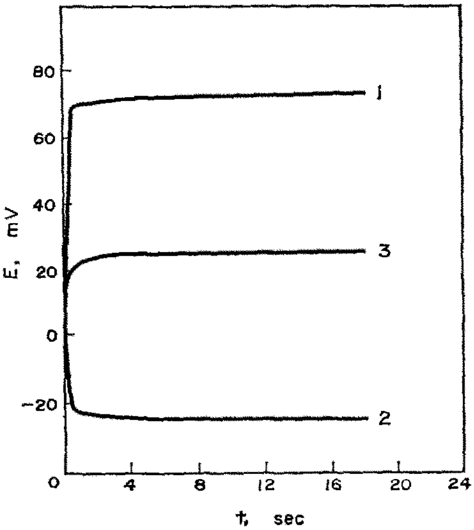


FIG. 3.—Response speed of the membrane-electrode. *1*—Ag^+; *2*—Tl^+; *3*—Hg_2^{2+}.

Department of Analytical Chemistry
University of Cluj, Cluj, Romania

C. LITEANU
ELENA HOPÎRTEAN

Summary—Results obtained by use of the PVC + tricresyl phosphate membrane-electrode in potentiometric precipitation titration of some halides and pseudohalides are given. Solutions of Ag^+, Tl^+ and Hg_2^{2+} were used as titrants, to which the membrane is responsive. The fast response to Ag^+ ions allowed the determination of iodide by automatic recording of the potentiometric curve (or its derivative).

Zusammenfassung—Mit der Membranelektrode aus PVC + Trikresylphosphat erhaltene Ergebnisse potentiometrischer Fällungstitrationen einiger Halogenide und Pseudohalogenide werden mitgeteilt. Lösungen von Ag^+, Tl^+ und Hg_2^{2+} wurden als Titranten verwendet; auf diese spricht die Membran an. Das schnelle Ansprechen auf Ag^+-Ionen erlaubte die Bestimmung von Jodid durch automatische Aufzeichnung der potentiometrischen Kurve (oder ihrer Ableitung).

Résumé—On donne les résultats obtenus par l'emploi de l'électrode membrane PVC + phosphate de tricrésyle dans le titrage potentiométrique par précipitation de quelques halogénures et pseudo-halogénures. Des solutions de Ag^+, Tl^+ et Hg_2^{2+} auxquelles la membrane répond ont été utilisées comme agents de titrage. La réponse rapide aux ions Ag^+ a permis le dosage de l'iodure par enregistrement automatique de la courbe potentiométrique (ou de sa dérivée).

REFERENCES

1. C. Liteanu and E. Hopîrtean, *Rev. Roumaine Chim.*, 1970, **15**, 749.
2. *Idem*, *Talanta*, 1970, **17**, 1067.
3. *Idem*, *Rev. Roumaine Chim.*, 1970, **15**, 1331.
4. *Idem*, *Studia Univ. "Babes-Bolyai"*, *Chem.*, 1970, **15**, 41.
5. *Idem*, *Rev. Roumaine Chim.*, 1971, **16**, 55.
6. C. Liteanu, E. Hopîrtean and M. Mioşcu, *Proc. III Analyt. Chem. Conf.*, *Budapest*, 1970, 35.
7. C. Liteanu and E. Hopîrtean, *Studia Univ. "Babes-Bolyai"*, *Chem.*, 1971, **16**, 83.
8. *Idem*, *Rev. Roumaine Chim.*, 1971, **16**, 559.
9. F. L. Hahn and G. Weiler, *Z. Anal. Chem.*, 1926, **69**, 417.

Talanta, 1972, Vol. 19, pp. 974 to 979. Pergamon Press. Printed in Northern Ireland

Use of membranes for equivalence point indication—VIII*
Electrochemical characterization of $BaSO_4$-parchment membrane-electrode

(*Received* 24 *June* 1971. *Accepted* 27 *November*)

THE ELECTROCHEMICAL characterization of ion-selective membrane-electrodes presumes the establishment of the factors which affect the electrode function, the selectivity, and the speed of response of the electrode.[1]

We have measured the electrode potential, speed of response, and impedance, under different experimental conditions, in order to obtain more thorough knowledge of the H^+-selective $BaSO_4$-parchment membrane-electrode.[2-4]

EXPERIMENTAL

The electrode function

The apparatus is shown in Fig. 1. The cell (with transport) can be represented by

(+) SCE	satd. KCl bridge	internal soln. 0·05*N* $Ba(OH)_2$	membrane	external soln. H_2SO_4, *xN*	satd. KCl bridge	SCE (−)	(1)

The pH-dependence of the membrane-electrode potential at 25 ± 0·1° was established by measuring the e.m.f. of cell (1) by means of an electronic potentiometer while the solution was being stirred. The results obtained, each the mean of 4 measurements with each of two electrodes, are represented in Fig. 2 (curve 1) for 10^{-6}–4*N* sulphuric acid. Membrane potentials were also measured at constant ionic strength ($I = 0{\cdot}075$; Fig. 2, curve 2).

---

* Part VII, *Stud. Univ. Babes-Bolyai, Chem.*, 1971, **16**, 25.

fast response to Ag^+ ions allowed the determination of iodide by automatic recording of the potentiometric curve (or its derivative).

Zusammenfassung—Mit der Membranelektrode aus PVC + Trikresylphosphat erhaltene Ergebnisse potentiometrischer Fällungstitrationen einiger Halogenide und Pseudohalogenide werden mitgeteilt. Lösungen von Ag^+, Tl^+ und Hg_2^{2+} wurden als Titranten verwendet; auf diese spricht die Membran an. Das schnelle Ansprechen auf Ag^+-Ionen erlaubte die Bestimmung von Jodid durch automatische Aufzeichnung der potentiometrischen Kurve (oder ihrer Ableitung).

Résumé—On donne les résultats obtenus par l'emploi de l'électrode membrane PVC + phosphate de tricrésyle dans le titrage potentiométrique par précipitation de quelques halogénures et pseudo-halogénures. Des solutions de Ag^+, Tl^+ et Hg_2^{2+} auxquelles la membrane répond ont été utilisées comme agents de titrage. La réponse rapide aux ions Ag^+ a permis le dosage de l'iodure par enregistrement automatique de la courbe potentiométrique (ou de sa dérivée).

REFERENCES

1. C. Liteanu and E. Hopîrtean, *Rev. Roumaine Chim.*, 1970, **15**, 749.
2. *Idem*, *Talanta*, 1970, **17**, 1067.
3. *Idem*, *Rev. Roumaine Chim.*, 1970, **15**, 1331.
4. *Idem*, *Studia Univ. "Babes-Bolyai"*, *Chem.*, 1970, **15**, 41.
5. *Idem*, *Rev. Roumaine Chim.*, 1971, **16**, 55.
6. C. Liteanu, E. Hopîrtean and M. Mioşcu, *Proc. III Analyt. Chem. Conf.*, *Budapest*, 1970, 35.
7. C. Liteanu and E. Hopîrtean, *Studia Univ. "Babes-Bolyai"*, *Chem.*, 1971, **16**, 83.
8. *Idem*, *Rev. Roumaine Chim.*, 1971, **16**, 559.
9. F. L. Hahn and G. Weiler, *Z. Anal. Chem.*, 1926, **69**, 417.

Talanta, 1972, Vol. 19, pp. 974 to 979. Pergamon Press. Printed in Northern Ireland

Use of membranes for equivalence point indication—VIII[*] Electrochemical characterization of $BaSO_4$-parchment membrane-electrode

(*Received* 24 *June* 1971. *Accepted* 27 *November*)

THE ELECTROCHEMICAL characterization of ion-selective membrane-electrodes presumes the establishment of the factors which affect the electrode function, the selectivity, and the speed of response of the electrode.[1]

We have measured the electrode potential, speed of response, and impedance, under different experimental conditions, in order to obtain more thorough knowledge of the H^+-selective $BaSO_4$-parchment membrane-electrode.[2-4]

EXPERIMENTAL

The electrode function

The apparatus is shown in Fig. 1. The cell (with transport) can be represented by

(+) SCE	satd. KCl bridge	internal soln. 0·05*N* $Ba(OH)_2$	membrane	external soln. H_2SO_4, xN	satd. KCl bridge	SCE (−)	(1)

The pH-dependence of the membrane-electrode potential at 25 ± 0·1° was established by measuring the e.m.f. of cell (1) by means of an electronic potentiometer while the solution was being stirred. The results obtained, each the mean of 4 measurements with each of two electrodes, are represented in Fig. 2 (curve 1) for 10^{-6}–4*N* sulphuric acid. Membrane potentials were also measured at constant ionic strength ($I = 0{\cdot}075$; Fig. 2, curve 2).

---

[*] Part VII, *Stud. Univ. Babes-Bolyai, Chem.*, 1971, **16**, 25.

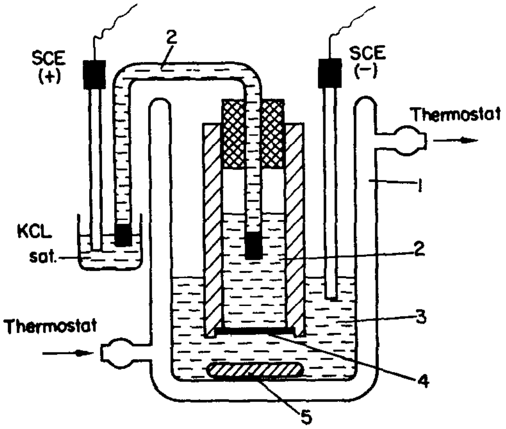


FIG. 1.—Schematic diagram of the measuring cell.
1—Double wall cell; 2—internal solution;
3—external solution; 4—membrane; 5—magnetic stirrer.

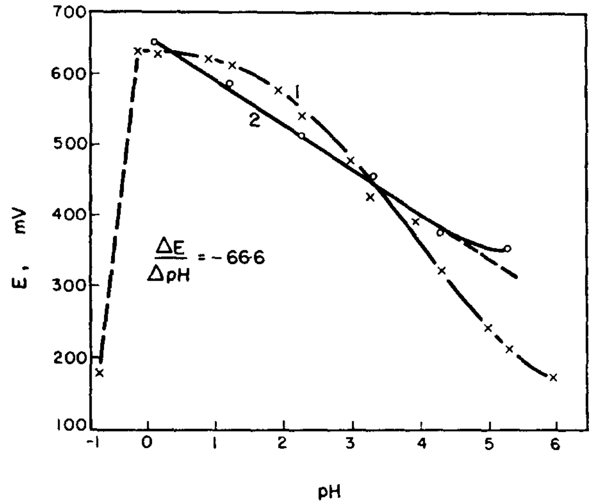


FIG. 2.—The electrode function E vs. pH.
1—Variable ionic strength.
2—Constant ionic strength (0·1).

Selectivity of the electrode

The ionic strength of the external solution was adjusted with sodium sulphate. It was therefore necessary to determine the influence of sodium ions on the electrode, by measuring the e.m.f. of the following cell (with transport):

(+) SCE	satd. KCl bridge	internal soln. 0·05N $Ba(OH)_2$	membrane	external soln. 0·05N H_2SO_4 xN Na_2SO_4	satd. KCl bridge	SCE (−)	(2)

Sodium sulphate solution (10^{-6}–$10^{-1}N$) had no effect on the electrode potential at 25°.

The temperature coefficient

The electrode functions best if the concentrations of the external and internal solutions are equal.[2-4] Therefore measurements of electrode potential as a function of temperature were made with 0·05*N* sulphuric acid as external solution and 0·05*N* barium hydroxide as internal solution. Results (mean values as above) are presented in Fig. 3.

Speed of response

A recording electronic potentiometer with small response inertia (Radelkis OH-102) was used to record the potential change when the electrode was immersed in a stirred 0·05*N* sulphuric acid solution at 25 ± 0·1°. The electrode (internal solution: 0·05*N* barium hydroxide) was equilibrated beforehand in sulphuric acid of concentrations 10^{-3}, 5×10^{-4}, 10^{-4}, 5×10^{-5}, 10^{-5}, 5×10^{-6} and $10^{-6}N$. In Fig. 4 a typical *E vs. t* curve is presented (curve 1), together with its linearization in co-ordinates $\log(E_\infty - E_t)$ *vs.* $\sqrt{t}$ (curve 2).

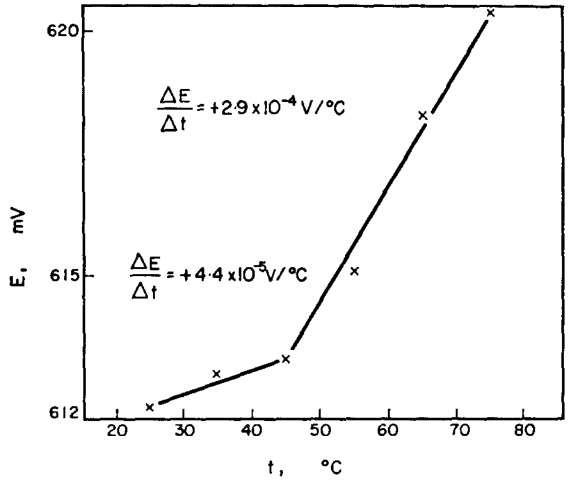


FIG. 3.—The temperature-dependence of the electrode potential.

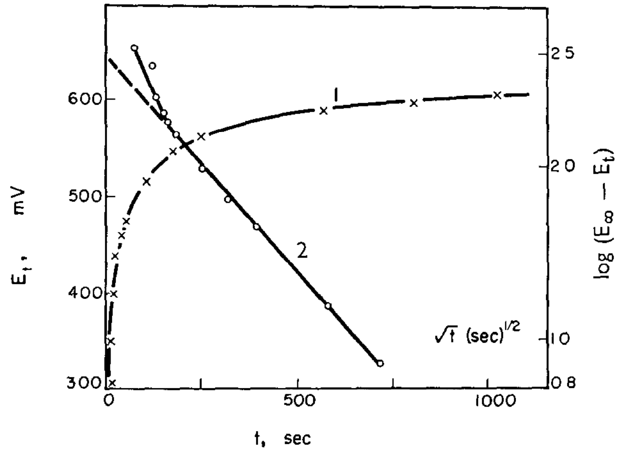


FIG. 4.—The time-dependence of the electrode potential.
1—*E vs. t.*
2—Linearization of the *E vs. t* function.

TABLE I.—MEAN SLOPE (k) OF LINEARIZED POTENTIAL *vs.* TIME CURVES.

	$(k \pm ts_k) \times 100$,*			
Concentration step $[H_2SO_4]$, N	25°C	45°C	65°C	$Ba(OH)_2$ 0·1N
$10^{-3} \rightarrow 5 \times 10^{-2}$	4·9 ± 0·9	5·8 ± 0·8	11·9 ± 0·2	6·9 ± 0·1
$5 \times 10^{-4} \rightarrow 5 \times 10^{-2}$	5·5 ± 0·3			
$10^{-4} \rightarrow 5 \times 10^{-2}$	4·7 ± 0·5			
$5 \times 10^{-5} \rightarrow 5 \times 10^{-2}$	5·6 ± 0·2			
$10^{-5} \rightarrow 5 \times 10^{-2}$	6·5 ± 1·3			
$5 \times 10^{-6} \rightarrow 5 \times 10^{-2}$	6·7 ± 0·2			
$10^{-6} \rightarrow 5 \times 10^{-2}$	6·9 ± 0·6			

* Three degrees of freedom confidence limit $\alpha = 0{\cdot}95$ (Student's $t = 3{\cdot}18$); s_k = standard deviation.

Table I gives the mean of 4 measurements, (2 with each of 2 electrodes) of speed of response of the electrode, in terms of the slope of the linearized E *vs.* t curves ($t > 30$ sec). The speed of response was also measured with the sulphuric acid heated to 45° and 65°, and for 0·1N barium hydroxide as the internal solution.

Impedance of the electrode

The membrane-electrode was connected in the assembly shown in Fig. 5. The signal generator (Tesla BM 314) gave a sinusoidal signal with amplitude 1·5 V. By means of the ellipse method with an oscillograph (Orion EMG Type/15380), the impedance and the phase-displacement angle were determined as a function of frequency. Figure 6 shows the results for impedance (curve 1) and for phase-displacement angle (curve 2).

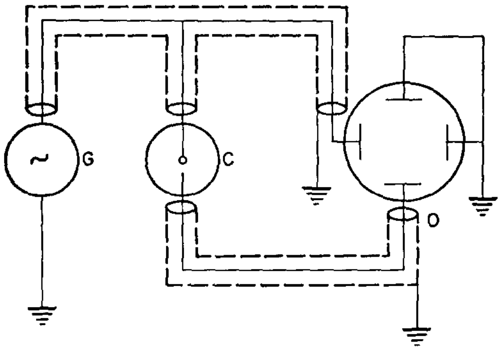


FIG. 5.—The experimental device for impedance measurements.
G, signal generator (TESLA BM-344).
C, measuring cell.
O, oscillograph (ORION EMG-1538/C).

The impedance of the electrode has been resolved into the capacitive (Z_c) and the reactive (Z_R) components.[5-7] Reciprocal variation of these components is shown in Fig. 7.

DISCUSSION

Electrode function

The parchment membrane-electrode, impregnated with barium sulphate, is well known to be a proton-selective electrode.[2,3] The slope of the E *vs.* pH plot has been evaluated as 65 mV at 25°, by titration of sulphuric acid with sodium hydroxide. This meant recording the electrode function at constant ionic strength. This explains the behaviour of the electrode as shown in Fig. 2. In curve 2, the slope reaches 66·6 mV per pH unit, in good agreement with the earlier result.

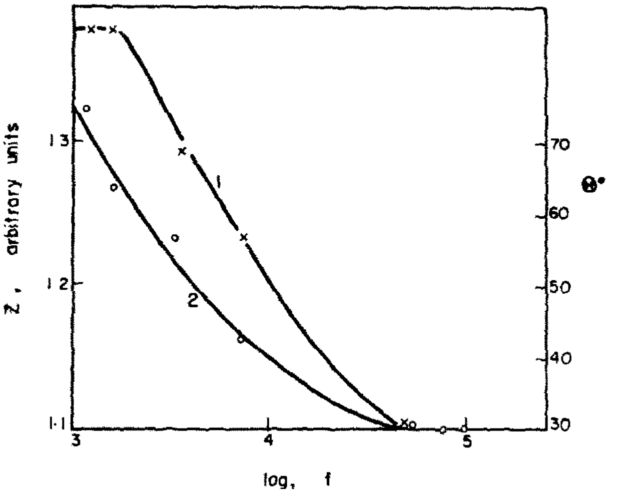


Fig. 6.—The dependence on log f, of (1) the impedance Z, (2) the phase-displacement angle θ.

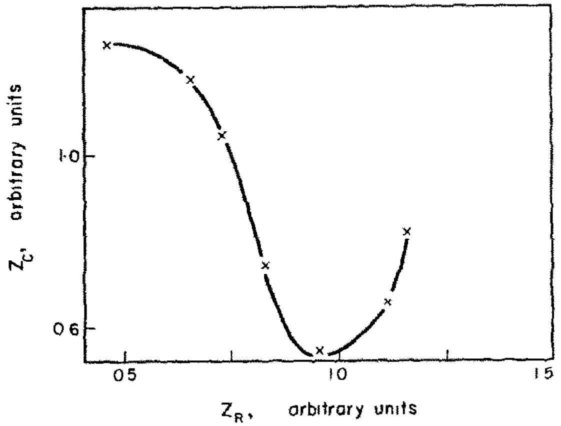


Fig. 7.—Relationship between Z_c and Z_R.

Selectivity of the electrode

It was found that the improvement in the behaviour of the electrode when it is operated at constant ionic strength is not the result of interference by sodium ions, so the electrode works on the basis of selective diffusion. The more dense the ion layer adsorbed on the barium sulphate surface, the more selective the electrode. This is the explanation for the increasing slope ($\Delta E/\Delta pH$) observed in curve 1 of Fig. 2.

The behaviour of the electrode at high temperatures offers further evidence in support of this hypothesis. Thus, at not too high temperatures the electrode has a temperature coefficient (88 $\mu V/K$) that is lower than the Nernstian value. Above a certain temperature (45°) diffusion ceases to be selective, and the temperature coefficient changes its value.

Speed of response

The process of reaching the equilibrium potential is generally slow. It proceeds in two stages: the first, electrical in nature, is rapid, and the second is slower and diffusional in nature, which is proved by the shape of the equation describing the E *vs.* t curve:

$$E_\infty - E_t = \text{const.}\, e^{-k\sqrt{t}} \qquad (3)$$

The facts that k is independent of the concentration of the pre-equilibrating solution, and that it increases in value with increasing temperature of the external solution and with increasing concentration of the internal solution support this explanation.

Impedance of the electrode

Though the experimental results are incomplete (the sensitivity of the apparatus is too low to allow exploration of the whole frequency range), it can be deduced, by analogy with glass electrodes, that presumably there is a layer on the surface of the parchment electrode that is different from the inside of the membrane. This is probably formed of barium sulphate on which sulphate ions are adsorbed. The existence of this layer is consistent with results on investigations on the formation of the electrode,[8–10] as well as with silver ions.[11]

It can be stated with certainty that the H^+-selective membrane-electrode made of parchment impregnated with barium sulphate works on the basis of a selective diffusion process.

Department of Analytical Chemistry
University of Cluj, Cluj, Romania

CANDIN LITEANU
IONEL CATALIN POPESCU

Summary—Some new aspects of the electrochemical characterization of the $BaSO_4$-parchment membrane-electrode are discussed. The electrode function E *vs.* pH is strongly affected by the ionic strength of the external solution. The electrode is mainly selective for hydrogen, and without interference from sodium ions. The basis of operation of the electrode is selective diffusion. This conclusion is supported by the temperature coefficient, the response rate, and the impedance measurements.

Zusammenfassung—Einige neue Aspekte der elektrochemischen Charakterisierung der Membranelektrode aus $BaSO_4$ und Pergament werden diskutiert. Die Elektrodenfunktion E(pH) wird durch die Ionenstärke der Außenlösung stark beeinflußt. Die Elektrode ist im wesentlichen selektiv für Wasserstoff und wird durch Natriumionen nicht gestört. Die Wirksamkeit der Elektrode beruht auf selektiver Diffusion. Dieser Schluß wird durch den Temperaturkoeffizienten, die Ansprechgeschwindigkeit und durch Impedanzmessungen gestützt.

Résumé—On discute de quelques nouveaux aspects de la caractérisation électrochimique de l'électrode-membrane $BaSO_4$-parchemin. La fonction d'électrode E par rapport au pH est fortement affectée par la force ionique de la solution externe. L'électrode est principalement sélective pour l'hydrogène, et sans interférence des ions sodium. La base de fonctionnement de l'électrode est la diffusion sélective. Cette conclusion est étayée par les mesures de coefficient de température, de la vitesse de réponse et de l'impédance.

REFERENCES

1. R. A. Durst, ed., *Ion-Selective Electrodes*, Chap. 11. Natl. Bur. Stds. Spec. Publ. 314, 1969.
2. P. Hirsch-Ayalon, *Rec. Trav. Chim.*, 1956, **75**, 1065.
3. *Idem, ibid*, 1960, **79**, 383.
4. *Idem, ibid*, 1961, **80**, 365.
5. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1185.
6. *Idem, ibid.*, 1969, **41**, 1788.
7. *Idem, ibid.*, 1970, **42**, 478.
8. C. Liteanu and M. Mioşcu, *Rev. Roumaine Chim.*, 1965, **10**, 903.
9. *Idem, ibid*, 1966, **11**, 863.
10. *Idem, ibid*, 1968, **13**, 209.
11. C. Liteanu and I. C. Popescu, *ibid.*, 1970, **15**, 973.

Talanta, 1972, Vol. 19, pp. 980 to 984. Pergamon Press. Printed in Northern Ireland

Conductometric titration with indicating resistance—III* Mechanism of the PVC + Alassion CS (Cationite R-H) + dioctyl phthalate (plasticizer) membrane as indicating resistance

(*Received* 14 *June* 1971. *Accepted* 5 *January* 1972)

THE END-POINT of conductometric acid–base titrations can be detected even when a highly conducting medium is used, if they are done in the presence of an indicating membrane.[1,2] In the presence of an ion-exchange membrane, the equivalence point is marked by a sudden decrease in the conductivity of the solution.

A previous paper[1] discussed the titration of hydrochloric acid in the presence of the membrane obtained by the plasticization of a mixture of PVC + Alassion CS + dioctyl phthalate at 140°. The present paper discusses the mechanism by which a similar membrane (PVC + Alassion CS + dioctyl phthalate, 2:1:4, plasticized at 175°) functions.

EXPERIMENTAL

The preparation of the membrane and the conductivity cell were described earlier.[2] Conductivities were measured with a Radelkis instrument with 300 and 80 Hz alternating current.

Hydrochloric acid (10^{-1}, 10^{-2}, 10^{-3} and $10^{-4}M$) in sodium chloride $5M$ was titrated with sodium hydroxide solutions ten times as concentrated as the acid, under equilibrium conditions (Fig. 1).

Recording the results under equilibrium conditions allows detection of the conductivity drop when a small excess of alkali is added. The time needed for the conductivity to become steady in the vicinity of the equivalence point and on first contact of the membrane with the acid solution to be analysed, varies between 30 min and 2 hr. The reversible exchange reaction

$$\text{R-H} + \text{Na}^+ \rightleftharpoons \text{RNa} + \text{H}^+ \qquad (1)$$

is shifted to the right at the equivalence point, and to the left initially. At other stages of the titration, the time necessary to establish equilibrium is 3–10 min. Before and after the equivalence point, the conductivity varies little. The general appearance of the curve is that of potentiometric curves, in contrast with the curves obtained in non-equilibrium conditions.[1]

Very low concentrations of acid may de determined, down to $10^{-4}N$. This concentration reduces the shift of the exchange equilibrium to the R-H form, giving a resistance change of only 50 Ω at the equivalence point. This change cannot be recorded in the case of a membrane with high resistance (2130 Ω, Fig. 1, curve *a*) but it can be if the membrane has a sufficiently low resistance, between 400 and 1300 Ω (1290 Ω, curve *b*, and 430 Ω, curve *c*). For acid concentrations higher than $10^{-3}N$ at the beginning of the titration, the exchange equilibrium is shifted further to the left, and thus the effect of the shift to the R-Na form is a change of about 600 Ω in resistance at the equivalence point and this variation can easily be measured whatever the resistance of the membrane (1140 Ω, curve *d*; 780 Ω, curve *e*; 578 Ω, curve *f*).

The conductivity of the membrane increases with the number of determinations (Fig. 2), the value also increasing inversely with the pH of the solutions. Solutions with initial pH between 3 and 4 give a membrane conductivity close of that obtained in neutral solutions. For acid solutions with initial pH below 3, the jump registered at the equivalence point of the titration represents a combination of two jumps, one occurring at pH 5–7 and the other at pH 9–11. The presence of the two jumps explains the non-superposition of curves *b* and *c* in Fig. 2.

The conductivity of $0{\cdot}01M$ hydrochloric acid in $5M$ sodium chloride is 21·45 $\Omega^{-1}.\text{m}^{-1}$. Introduction of a membrane between the electrodes decreases the conductivity. The decrease is not very large if the membrane is made without plasticizer, (*i.e.* only of PVC + Alassion CS, and obtained by dissolution of the polymer in tetrachlorethane), the conductivity then being 17·4 $\Omega^{-1}.\text{m}^{-1}$. For the same membrane thermally treated at 175°, the conductivity decreases to 13·1 $\Omega^{-1}.\text{m}^{-1}$. These conductivities

---

* Part II, *Rev. Roumaine Chim.*, 1970, **15**, 1871.

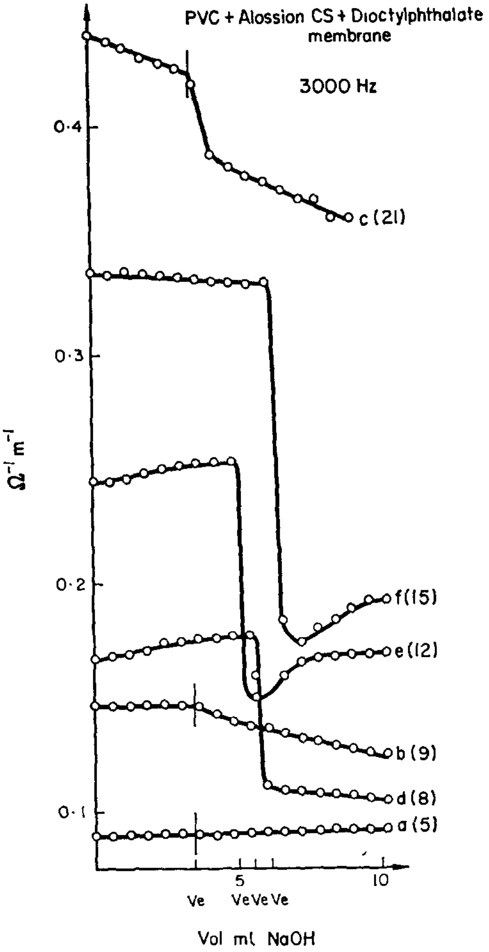


Fig. 1.—Curves *a*, *b*, *c*—titration of $10^{-4}M$ HCl + $5M$ NaCl with $10^{-3}N$ NaOH; *d*—titration of $10^{-3}M$ HCl + $5M$ NaCl with $10^{-2}M$ NaOH; *e*—titration of $10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH; *f*—titration of $10^{-1}M$ HCl + $5M$ NaCl with $1M$ NaOH. The figure in brackets gives the serial number of the determination in a set with the same membrane.

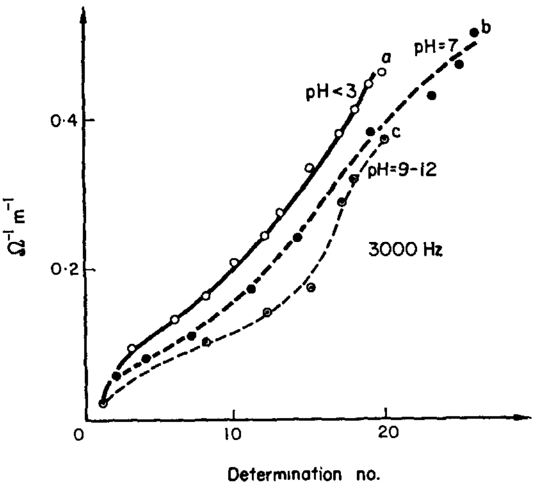


Fig. 2.—Variation of the conductivity of PVC + Alassion CS + dioctyl phthalate membrane with the number of determinations.

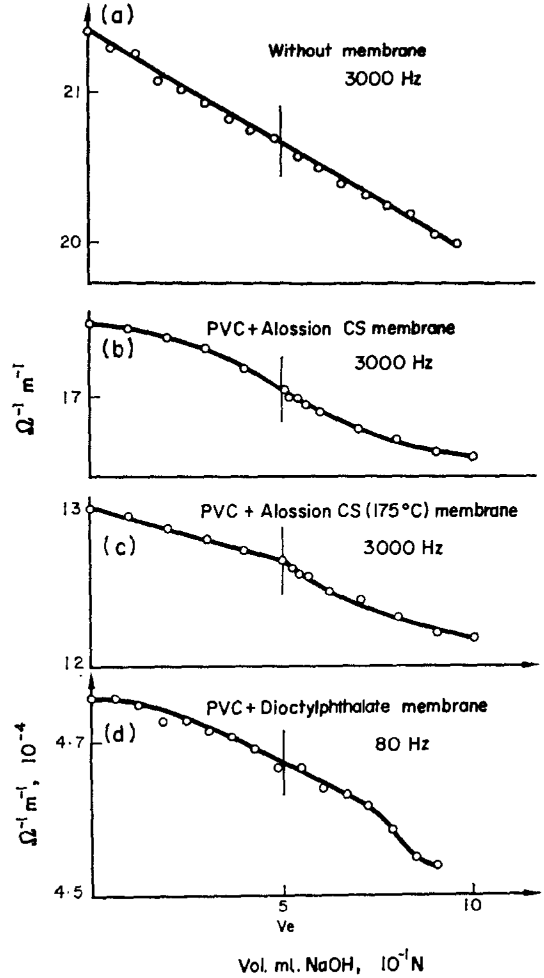


FIG. 3.—Conductometric titration curves of $10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH. Curve *a* without membrane; *b*, *c*, *d* with various membranes.

were measured under equilibrium conditions and do not vary with the number of determinations. A membrane without cation-exchanger, obtained from PVC + dioctyl phthalate, plasticized at 175°, diminishes the conductivity of the system by a factor of 10^4. The membrane PVC + Alassion CS + dioctyl phthalate decreases the conductivity a great deal (0·023 $\Omega^{-1}.m^{-1}$ in the first determination) and, as mentioned above, the conductivity increases with the number of determinations. When the conductivity of the membrane has increased to the optimum (determinations 5–20), it is about 1/100 that of the solution.

The transport of electricity in the membrane is performed by the exchange ions, which are held back to an extent determined by the exchange group, leading to a larger or smaller conductivity. Alassion CS is a strongly acidic cation-exchanger with sulphonic acid groups. In the case of a membrane formed only of PVC + Alassion CS, the exchange R-H + $Na^+ \rightleftharpoons$ R-Na + H^+ occurs also in the acid pH range. In such a membrane, after repeated treatment with $5M$ sodium chloride, the amount of H^+ unexchanged leads to an increase of the resistance by only 0·2 Ω when the membrane is in contact with alkali, whereas in the case of a solution with a 1 : 50 ratio of $[H^+]:[Na]$, the increase is 1·5–2 Ω. This change in conductivity at the equivalence point in the presence of alkali is insufficient for the membrane to be used as an indicating device, as shown by the appearance of a simple inflexion on the titration curve (Fig. 3, curves *b* and *c*). The PVC + dioctyl phthalate membrane has a particularly large resistance and an exchange of H^+ ions for Na^+ (decrease in conductivity) is observed only

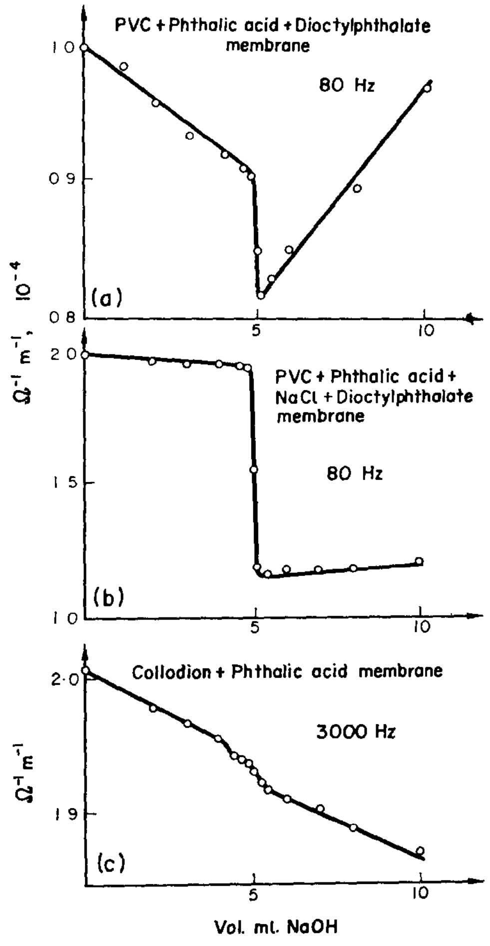


FIG. 4.—Conductometric titration curves of $10^{-2}M$ HCl + $5M$ NaCl with $10^{-1}M$ NaOH with different membranes containing phthalic acid.

at a very alkaline pH (Fig. 3, curve *d*). For these reasons the membrane formed only of PVC + plasticizer cannot be used as an indicator in acid-base titrations.

The indicator properties of the PVC + Alassion CS + dioctyl phthalate membrane (plasticized at 175°) can be explained by the existence of two types of protonated species in the membrane, with different dissociation constants, which give exchange of H^+ for Na^+ in two pH regions (5–7 and 9–11). These species arise as follows: at the membrane formation temperature (175°), dioctyl phthalate reacts with the sulphonic acid group of the ion-exchanger, forming octyl sulphonate and phthalic acid. The latter has two carboxylic groups with dissociation constants $K_1 = 1{\cdot}3 \times 10^{-3}$ and $K_2 = 3{\cdot}9 \times 10^{-6}$. The presence of phthalic acid in the membrane was proved on the basis of its optical properties, and the reaction of Alassion CS with dioctyl phthalate at the same temperature. A newly prepared membrane contains non-crystalline phthalic acid, since crystallization takes some time. The presence of phthalic acid right from the preparation of the membrane means that a conductivity jump will occur at the equivalence point, even in the first titrations. Esterification of the sulphonic acid grouping explains the low conductivity of the membrane immediately after its preparation. Slow hydrolysis of the sulphonate ester (*i.e.*, with repeated determinations) increases the number of ionogenic groups and hence the conductivity of the membrane. At the equivalence point both carboxylic groups of the phthalic acid can give ion-exchange, the first at pH 5–7, the second at pH 9–11, thus increasing the effect as the pH rises. As the number of determinations increases, some phthalic acid is dissolved out and the conductivity jump at the equivalence point decreases considerably. That is why, although the resistance of the membrane falls below 500 Ω, it cannot be used further for this purpose.

The role of the phthalic acid was deduced from experiments in which a homogeneous PVC + phthalic acid + dioctyl phthalate (3:1:4) membrane (plasticized at 175°) was used in the titration of 0·01*M* hydrochloric acid in 5*M* sodium chloride with 0·1*M* sodium hydroxide (Fig. 4, curve *a*). This membrane has a particularly high resistance. Introduction of sodium chloride (PVC + NaCl + phthalic acid + dioctyl phthalate: 4:1:1:8) diminishes its resistance a little, but the titration curve obtained is identical with that of the Alassion CS membrane (Fig. 4, curve *b*).

A membrane made of phthalic acid in collodion has a high conductivity, but is a poor indicator because of its heterogeneity. In such a membrane only a small part of the phthalic acid takes part in an exchange reaction, *viz.* that part dissolved by the ether of the collodion solution and recrystallized. The undissolved phthalic acid granules react only on the surface. The titration curve with a collodion + phthalic acid membrane indicates both the exchange steps of phthalic acid, though only by small conductivity changes (Fig. 4, curve *c*).

Dept. of Analytical Chemistry and
Dept. of Mineralogy
University of Cluj, Cluj, Romania

Candin Liteanu
Lucretia Ghergariu-Mîrza

Summary—The problem of conductometric acid–base titration in a highly-conducting medium (5*M* sodium chloride) has been solved by introducing a PVC + Alassion CS + dioctyl phthalate membrane between the two electrodes. The equivalence point is marked by a sudden decrease in conductivity. The membrane (obtained by plasticization at 175°) functions through the phthalic acid dissolved in the PVC membrane, this acid being formed by decomposition of the dioctyl phthalate by the sulphonic acid groups of the cation-exchanger. In this process the sulphonic acid groups are esterified, but hydrolyse on being treated for 2–3 hr with NaOH, and then increase the conductivity in the membrane.

Zusammenfassung—Das Problem der konduktometrischen Säure-Basen-Titration in einem gut leitenden Medium (5 M Natriumchlorid) wurde dadurch gelöst, daß eine Membran aus PVC + Alassion CS + Dioctylphthalat zwischen die Elektroden gesetzt wird. Der Äquivalenzpunkt macht sich durch einen plötzlichen Abfall in der Leitfähigkeit bemerkbar. Die durch Verpressen bei 175° hergestellte Membran ermöglicht diesen Effekt durch die im PVC gelöste Phthalsäure, die durch die Zersetzung des Dioctylphthalats an den Sulfonsäuregruppen des Kationenaustauschers entsteht. Bei diesem Prozeß werden die Sulfonsäuregruppen verestert; sie hydrolysieren jedoch bei 2–3-stündiger Behandlung mit NaOH. Dann erhöhen sie die Leitfähigkeit in der Membran.

Résumé—Le problème du titrage conductimétrique acide-base dans un milieu hautement conducteur (chlorure de sodium 5*M*) a été résolu en introduisant une membrane PVC + Alassion CS + phtalate de dioctyle entre les deux électrodes. Le point d'équivalence est marqué par un décroissement brusque en conductivité. La membrane (obtenue par plastification à 175°) fonctionne par l'intermédiaire de l'acide phtalique dissous dans la membrane en PVC, cet acide étant formé par la décomposition du phtalate de dioctyle par les groupes acide sulfonique de l'échangeur de cations. Dans ce processus les groupes acide sulfonique sont estérifiés, mais s'hydrolysent par traitement de 2–3 h par NaOH, accroissant la conductivité dans la membrane.

REFERENCES

1. C. Liteanu and E. Hopîrtean, *Rev. Roumaine Chim.*, 1967, **12**, 517.
2. C. Liteanu and L. Ghergariu-Mirza, *ibid.*, 1970 **15**, 1871.

Talanta, 1972, Vol. 19, pp. 985 to 988. Pergamon Press. Printed in Northern Ireland

Characterization of ceramic ion-selective membrane-electrodes—I
The Ag_2S electrode

(*Received* 9 *June* 1971. *Accepted* 27 *November* 1971)

SILVER SULPHIDE has been used for making homogeneous or heterogeneous silver-selective membrane-electrodes, the former by heating a mixture of silver halides and silver sulphide[1] or from single crystals of the sulphide[2–5] and the latter by using an inert material to bind the silver sulphide.[6–7]

The performance of heterogenous ion-selective membrane-electrodes (ISME) has been shown to be inferior to that of homogeneous ISME if silver sulphide is used as the electrochemically active material.[8] We have therefore tried to produce an easily fabricated homogeneous Ag^+-selective membrane-electrode.[9] In this paper the behaviour of a ceramic silver sulphide membrane as an Ag^+-selective electrode is described.

EXPERIMENTAL

Electrode

To one end of a "plexiglass" tube a ceramic Ag_2S disc was attached (Fig. 1). As inner solution, $0{\cdot}1M$ silver nitrate was used. The electrode potential was evaluated by means of the cell

(−) S.C.E.	$0{\cdot}1M$ KNO_3 agar-agar bridge	Internal solution $0{\cdot}1M$ $AgNO_3$	Membrane	External solution (test)	$0{\cdot}1M$ KNO_3 agar-agar bridge	S.C.E. (+)	(1)

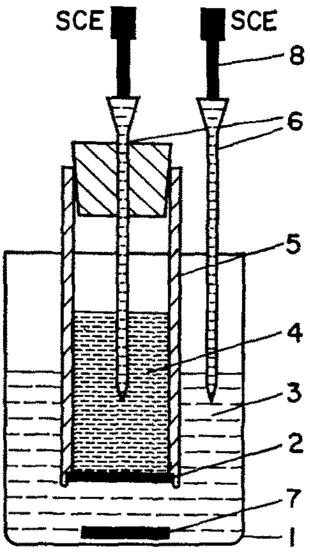


FIG. 1.—Schematic diagram of the working cell. 1—cell; 2—membrane; 3—external solution; 4—internal solution; 5—electrode body; 6—KNO_3 agar-agar bridge; 7—magnetic stirrer; 8—saturated calomel electrode.

Electrode response

Silver ions. With the ISME immersed in aqueous solutions (10^{-6}–$2M$) of silver nitrate, the electrode response was recorded with and without stirring. The electrode response is linear, but the slope is lower than the Nernstian value (64·6 mV with stirring, 50 mV without). These experiments were repeated at constant ionic strength (0·1*M*) maintained by addition of potassium nitrate. The slope is then within 2% of being Nernstian (58·2 mV). The activity response curve is parallel, but shifted on account of the activity coefficient of silver ions (the value[10] used was 0·61).

Mercury(II) ions. Since it is known that mercury(II) interferes seriously when this electrode is used, the ISME was tested for response to mercury(II), by similar methods. The response curve (for an ionic strength of 0·1*M*) is linear with Nernstian slope (30 mV). The activity response is parallel, the shift depending on the activity coefficient of mercury(II) (the value[10] 0·14 was used).

Selectivity

Mercury(II). To determine the selectivity constant of the electrode for Hg^{2+}, a variant of Rechnitz's method[11] was used. From the equations:

$$E_1 = E^\circ + 0{\cdot}0582 \log a_{Ag^+} \tag{2}$$

$$E' = E^\circ + 0{\cdot}0582 \log (a_{Ag^+} + K_{Ag^+,Hg^{2+}} . a^{1/2}_{Hg^{2+}}) \tag{3}$$

where $K_{Ag^+,Hg^{2+}}$ is the selectivity coefficient, we obtain

$$10^{(E'-E_1)/0{\cdot}0582} = 1 + K_{Ag^+,Hg^{2+}} . \frac{a^{1/2}_{Hg^{2+}}}{a_{Ag^+}} \tag{4}$$

When a_{Ag^+} and the ionic strength are kept constant, from a plot of $10^{(E'-E_1)/0{\cdot}0582}$ *vs.* $c^{1/2}_{Hg^{2+}}$ the selectivity coefficient can be obtained, if the individual activity coefficients of Hg^{2+} and Ag^+ are known. Results for a $5 \times 10^{-5}M$ Ag^+ solution titrates with a $10^{-2}M$ solution of Hg^{2+} which contains $5 \times 10^{-5}M$ Ag^+, at $I = 0{\cdot}1M$, are presented in Fig. 2.

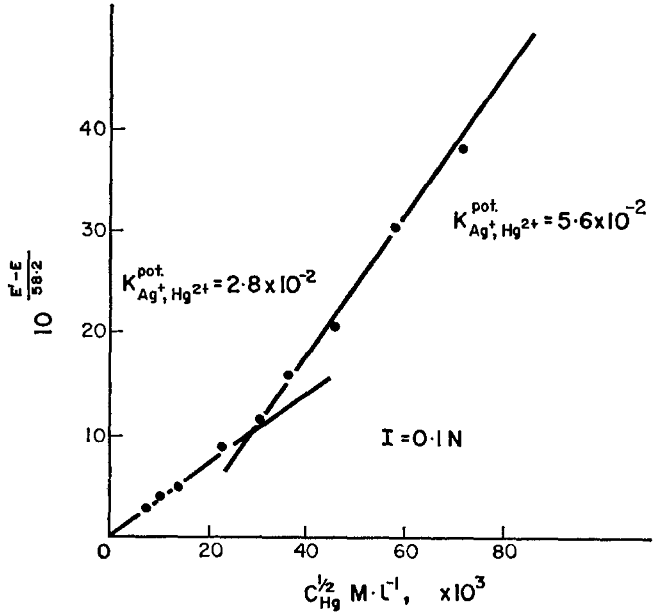


FIG. 2.—Plot of $10^{(E'-E_1)/58{\cdot}2}$ *vs.* $c^{1/2}_{Hg^{2+}}$ for $5 \times 10^{-5}M$ $AgNO_3$ with various additions of $10^{-2}M$ $Hg(NO_3)_2$ + $5 \times 10^{-5}M$ $AgNO_3$.

Copper(II). A faster but less accurate method[12] consists of electrode potential measurements in two solutions, of Ag^+ and of Cu^2, respectively, of the same activity. It follows from equation (3) that for $a_{Ag^+} = 0$,

$$E_2 = E^\circ + 0{\cdot}0582 \log K_{Ag^+;Cu^{2+}} . a^{1/2}_{Cu^{2+}} \tag{5}$$

By combining equations (2) and (5), we obtain

$$\log K_{\mathrm{Ag^+,Cu^{2+}}} = \frac{E_2 - E_1}{0{\cdot}0582} \tag{6}$$

Results of determinations for $c_{\mathrm{Ag^+}} = 0{\cdot}1M \equiv c_{\mathrm{Cu^{2+}}}$ gave $K_{\mathrm{Ag^+,Cu^{2+}}} = 10^{-5}$.

Hydrogen ions. Hydrogen ions must affect the electrode potential through acid-base equilibria in which the sulphide ion is involved. The electrode could indeed be used as an indicating electrode in acid-base titrations. Determination of the selectivity coefficient by the Rechnitz method[11] gave $K_{\mathrm{Ag^+,H^+}} = 10^{-5}$.

Reproducibility

Reproducibility of potential measurements was tested for 10^{-1}, 10^{-3} and $10^{-5}M$ silver (ionic strength $0{\cdot}1M$). The results were practically identical for 20 measurements in each case. The variation of the electrode potential does not exceed 1–2 mV over a period of 24 hr.

Applications

The electrode may be used with good results in the titration of silver with $\mathrm{Cl^-}$, $\mathrm{SCN^-}$, $\mathrm{Br^-}$ and $\mathrm{I^-}$ The potential jump at the equivalence point exceeds 200 mV for $\mathrm{Cl^-}$ and reaches 600 mV for $\mathrm{I^-}$. Titrations of mercury(II) with $\mathrm{Cl^-}$, $\mathrm{SCN^-}$, $\mathrm{Br^-}$ and $\mathrm{I^-}$ also give good results. The potential jump is particularly large (700–800 mV) in the titration of $\mathrm{Hg^{2+}}$ or $\mathrm{Ag^+}$ with $\mathrm{SH^-}$.

DISCUSSION

The membrane gives an electrode response closer to the theoretical for $\mathrm{Ag^+}$ and $\mathrm{Hg^{2+}}$, if the ionic strength is kept constant at a value equal to that of the salt bridges used, and this shows that the non-Nernstian response at variable ionic strength is due to the contribution of the diffusion potential, at the interfaces, to the e.m.f. of the cell. The influence of stirring also supports this view. The electrode is primarly $\mathrm{Ag^+}$-selective, with strong interference by $\mathrm{Hg^{2+}}$. Interference by other cations may be due either to precipitation of a sulphide more sparingly soluble than $\mathrm{Ag_2S}$, on the surface of the electrode, or to decomposition of the $\mathrm{Ag_2S}$ by sequestration of $\mathrm{Ag^+}$ or of $\mathrm{S^{2-}}$. Interference by precipitation has been detected in the case of $\mathrm{Hg^{2+}}$ and $\mathrm{Cu^{2+}}$. The response to hydrogen ions can be considered as the second type of interference. If the potential *vs.* pH relationship for this electrode in an acid–base titration is considered, the slope is about 25 mV per pH unit, confirming the assumption[4] that hydrogen ions interfere by protonating the sulphide ion.

Department of Analytical Chemistry
University of Cluj, Cluj,
Romania

Candin Liteanu
Ionel C. Popescu
Vladimir Ciovîrnache

Summary—The behaviour of a new type of electrode, made from ceramic $\mathrm{Ag_2S}$, has been investigated. The electrode response is Nernstian for $\mathrm{Ag^+}$ over the range 10^{-6}–$2M$ and for $\mathrm{Hg^{2+}}$ in the concentration range 10^{-6}–$10^{-2}M$, both at constant ionic strength (0.1M). The electrode is $\mathrm{Ag^+}$-selective, with maximum interference from $\mathrm{Hg^{2+}}$. It can be used for acid–base potentiometric titration and for potentiometric $\mathrm{Ag^+}$ and $\mathrm{Hg^{2+}}$ precipitation titrations.

Zusammenfassung—Das Verhalten eines neuen Elektrodentyps aus keramischem $\mathrm{Ag_2S}$ wurde untersucht. Das Verhalten der Elektrode entspricht mit $\mathrm{Ag^+}$ im Bereich 10^{-6}–$2M$ der Nernstschen Gleichung und mit $\mathrm{Hg^{2+}}$ bei 10^{-6}–$10^{-2}M$, jeweils bei konstanter Ionenstärke (0,1M). Die Elektrode ist selektive für $\mathrm{Ag^+}$ und wird am stärksten durch $\mathrm{Hg^{2+}}$ gestört. Sie kann zur potentiometrischen Säure-Basen-Titration und zu potentiometrischen Fällungstitrationen von $\mathrm{Ag^+}$ und $\mathrm{Hg^{2+}}$ verwendet werden.

Résumé—On a étudié le comportement d'un nouveau type d'électrode, fait de $\mathrm{Ag_2S}$ céramique. La réponse de l'électrode est Nernstienne pour $\mathrm{Ag^+}$ dans le domaine 10^{-6}–$2M$ et pour $\mathrm{Hg^{2+}}$ dans le domaine de concentration 10^{-6}–10^{-2} M, tous deux à force ionique constante (0,1M). L'électrode est sélective pour $\mathrm{Ag^+}$, avec interférence maximale de $\mathrm{Hg^{2+}}$. Elle peut être utilisée pour le titrage potentiométrique acide-base et pour les titrages par précipitation de $\mathrm{Ag^+}$ et $\mathrm{Hg^{2+}}$.

REFERENCES

1. E. M. Shobets and G. A. Kleibst, *J. Gen. Chem., USSR*, 1948, **10**, 1612.
2. Sulphide Specific Ion Electrode, Orion Model 94-16, *Applications Bulletin*, No. 3 and No. 12.
3. T. S. Light and J. L. Swartz, *Anal. Lett.*, 1968, **1**, 825
4. T. M. Hseu and G. A. Rechnitz, *Anal. Chem.*, 1968, **40**, 1054.
5. R. Bock and H. J. Puff, *Z. Anal. Chem.*, 1968, **240**, 381.
6. Sulphide Selective Membrane Electrode, Radelkis Type OP-S-711, *The Application of Ion-Selective Membrane Electrodes*. Radelkis, Budapest 1968.
7. M. Mascini and A. Liberti, *Anal. Chim. Acta*, 1970, **51**, 231.
8. N. Bottazzini and V. Crespi, *Chim. Ind.*, 1970, **52**, 866.
9. C. Liteanu, I. C. Popescu and S. B. Domşa, *Roumanian Patent*, 1971.
10. *Guide to Selective Ion Electrodes Measurements*, p. 16. Beckman, Instruments.
11. K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, 1969, **41**, 1203.
12. G. Eisenman, D. O. Rudin and J. O. Casby, *Science*, 1957, **126**, 831.

Talanta, 1972, Vol. 19, pp. 989 to 1007. Pergamon Press. Printed in Northern Ireland

VOLTAMMETRY IN DIMETHYLSULPHOXIDE—A REVIEW

THOMAS R. KOCH* and WILLIAM C. PURDY
Department of Chemistry, University of Maryland, College Park, Md. 20742, U.S.A.

(*Received* 15 *November* 1971. *Accepted* 27 *December* 1971)

Summary—A review is given of voltammetric studies using dimethylsulphoxide as supporting electrolyte, and includes details of inorganic and organic systems studied and of the reference electrodes developed for use in this medium.

IN RECENT YEARS the scope of voltammetry has been expanded by an increase in the number of non-aqueous solvents employed. Dimethylsulphoxide (DMSO) has been of great value in these voltammetric studies owing to its high dielectric constant and absence of ionizable protons. Many investigators have found purification of the solvent to be a necessity, owing to a cathodic wave caused by an impurity. This impurity can be removed by distillation; in addition, distillation over a drying agent helps to ensure a constant, low water level (usually about 0·03–0·05%). Tetra-alkylammonium salts are generally employed as supporting electrolytes to take full advantage of the extended cathodic range of DMSO as compared to water. While a variety of reference electrodes have been used, the most common is an aqueous saturated calomel electrode (SCE), separated from the sample compartment by a salt bridge. Several reference electrodes employing DMSO as a solvent have been described and they will be discussed later.

EARLIER WORK

The first voltammetric studies in DMSO were conducted in 1959 by Gutmann and Schöber.[1] With tetraethylammonium nitrate as supporting electrolyte, they reported a usable voltage range from −0·2 to −2·74 *vs.* SCE. These workers described the frequent occurrence of maxima which, in some cases, were at least partially eliminated by varying the drop-rate. Conventional and derivative polarographic methods were used. Single, well-defined waves were found for the alkali metal ions and for the ammonium ion. The alkaline-earth metal ions were reported to give single, well-defined waves. Silicon tetrachloride exhibited two waves, well-formed and of equal height. Zirconium(IV) and hafnium(IV) gave well-developed waves, each exhibiting a small first-order maximum. Titanium(IV) gave a wave which was ideal in shape; derivative polarography showed three indistinct steps in this reduction, corresponding to

$$\mathrm{Ti(IV)} \rightarrow \mathrm{Ti(III)} \rightarrow \mathrm{Ti(II)} \rightarrow \mathrm{Ti(0)}.$$

Antimony(III) exhibited three waves and niobium(V) one. The half-wave potential values reported by Gutmann and Schöber are included in Table I. These authors carried out no concentration studies. However, by use of a variety of reference

---

* Present address: Erie County Laboratories, E. J. Meyer Memorial Hospital Division, 462 Grider Street, Buffalo, N.Y. 14214, U.S.A.

TABLE I.—POLAROGRAPHIC DATA IN DMSO. A. INORGANIC MATERIALS

Active species	Form used	Inert electrolyte	$-E_{1/2}$, V	Reference electrode	T, °C	Ref.	Miscellaneous
Al(III)	$Al(ClO_4)_3$	0·1*M* TEAP	1·67(1) 1·95(2)	Ag/DMSO	?	35	$n_1 + n_2 = 2{\cdot}90$ $I_1 = 0{\cdot}86$; $I_2 = 1{\cdot}19$
Al(III)	$AlCl_3$	0·1*M* TEAP	1·5	SCE	25	14	
Ba(II)	$Ba(ClO_4)_2$	0·1*M* TEAP	1·95	Ag/DMSO	?	35	$n = 1{\cdot}97$; $I = 2{\cdot}07$
Ba(II)	$BaCl_2$	0·1*M* $TEANO_3$	2·09	SCE	21	1	
Ca(II)	$Ca(NO_3)_2$	0·1*M* $TEANO_3$	2·30	SCE	21	1	
Ca(II)	$Ca(ClO_4)_2$	0·1*M* TEAP	2·38	Ag/DMSO	?	35	$n = 0{\cdot}96$; $I = 1{\cdot}48$
Cd(II)	$Cd(ClO_4)_2$	0·1*M* TEAP	0·58	Ag/DMSO	?	35	$n = 1{\cdot}84$; $I = 1{\cdot}88$
Cd(II)	$Cd(ClO_4)_2$	0·1*M* TBAP	0·931	Hg Pool	35	11	$m = 0{\cdot}033$; $D = 6{\cdot}75$
Cd(II)	$Cd(ClO_4)_2$	0·1*M* TBAP	0·966	Hg Pool	25	11	$m = 0{\cdot}032$; $D = 4{\cdot}94$
Cd(II)	$Cd(ClO_4)_2$	0·1*M* $KClO_4$	0·820	Hg Pool	25	11	$D = 4{\cdot}35$
Cd(II)	$Cd(ClO_4)_2$	0·1*M* $KClO_4$	0·820	SCE	25	11	$m = 0{\cdot}030$
Cd(II)	$Cd(NO_3)_2$	0·1*M* $KClO_4$	0·63	SCE	25	9	
Cd(II)	$Cd(ClO_4)_2$	1·0*M* $KClO_4$	0·789	Hg Pool	25	11	$m = 0{\cdot}040$
Cd(II)	$Cd(ClO_4)_2$	1·0*M* $KClO_4$	0·794	Hg Pool	35	11	$m = 0{\cdot}048$; $D = 2{\cdot}52$
Cd(II)	$Cd(ClO_4)_2$	1·0*M* $KClO_4$	0·685	SCE	25	11	$m = 0{\cdot}031$; $D = 1{\cdot}66$
Cd(II)	$Cd(ClO_4)_2$	1·0*M* $KClO_4$	0·670	SCE	35	11	$m = 0{\cdot}047$
Cd(II)	$Cd(NO_3)_2$	1·0*M* $KClO_4$	0·66	SCE	25	9	$m = 0{\cdot}029$
Ce(III)	$CeCl_3$	0·1*M* TEAP	2·24	SCE	21	7	$n = 3$
Co(II)	$Co(NO_3)_2$	0·1*M* TBAP	1·43	SCE	25	9	
Co(II)	$Co(ClO_4)_2$	0·1*M* TEAP	1·28	Ag/DMSO	?	35	$I = 1{\cdot}96$; $n = 1{\cdot}78$
Co(II)	$Co(ClO_4)_2$	0·1*M* $KClO_4$	1·316	SCE	25	11	
Co(II)	$Co(ClO_4)_2$	1·0*M* $KClO_4$	1·465	SCE	25	11	$m = 0{\cdot}096$; $D = 0.734$
Co(II)	$Co(ClO_4)_2$	1·0*M* $KClO_4$	1·423	SCE	35	11	$m = 0{\cdot}100$
Co(II)	$Co(ClO_4)_2$	1·0*M* $KClO_4$	1·520	Hg Pool	25	11	$m = 0{\cdot}130$; $D = 4{\cdot}83$
Co(II)	$Co(ClO_4)_2$	1·0*M* $KClO_4$	1·536	Hg Pool	35	11	$m = 0{\cdot}097$; $D = 1{\cdot}06$
Cr(III)	$Cr(ClO_4)_3$	0·1*M* $KClO_4$	0·822(1) 1·556(2)	SCE	25	11	$D = 0{\cdot}938$
Cr(III)	$Cr(ClO_4)_3$	1·0*M* $KClO_4$	0·870(1) 1·603(2)	SCE	25	11	
Cs(I)	CsCl	0·1*M* $TEANO_3$	2·03	SCE	21	1	
Cu(II)	$Cu(ClO_4)_2$	0·1*M* TBAP	0·341	Hg Pool	25	11	$m = 0{\cdot}130$; $D = 4{\cdot}83$
Cu(II)	$Cu(ClO_4)_2$	0·1*M* TEAP	—0·05	Ag DMSO	?	35	$n = 1{\cdot}95$; $I = 1{\cdot}95$
Cu(II)	$Cu(ClO_4)_2$	0·1*M* $KClO_4$	0·212	Hg Pool	25	11	$m = 0{\cdot}121$; $D = 7{\cdot}12$

Cu(II)	$Cu(ClO_4)_2$	1·0*M* $KClO_4$	0·127	Hg Pool	25	11	$m = 0{\cdot}100$
Cu(II)	$Cu(ClO_4)_2$	1·0*M* $KClO_4$	0·122	Hg Pool	35	11	$m = 0{\cdot}103$; $D = 2{\cdot}46$
Cu(II)	$Cu(ClO_4)_2$	1·0*M* $KClO_4$	0·058	SCE	25	11	$m = 0{\cdot}102$; $D = 1{\cdot}73$
Cu(II)	$Cu(ClO_4)_2$	1·0*M* $KClO_4$	0·051	SCE	35	11	$m = 0{\cdot}127$
Dy(III)	$DyCl_3$	0·1*M* TEAP	2·08	SCE	21	7	$n = 3$
Er(III)	$ErCl_3$	0·1*M* TEAP	2·09	SCE	21	7	$n = 3$
Eu(III)	$EuCl_3$	0·1*M* TEAP	0·81(1) 2·12(2)	SCE	21	7	$n_1 = 1$; $n_2 = 2$
Fe(II)	$Fe(ClO_4)_2$	0·1*M* TEAP	1·12	Ag/DMSO	?	35	$n = 1{\cdot}60$
Fe(III)	$Fe(ClO_4)_3$	0·1*M* TEAP	−0·05(1) 1·12(2)	Ag/DMSO	?	35	$n_1 = 0{\cdot}80$; $n_2 = 1{\cdot}20$
Fe(III)	$Fe(ClO_4)_3$	0·1*M* $KClO_4$	0·722(1) 1·411(2)	SCE	25	11	$m_1 = 0{\cdot}037$; $D = 1{\cdot}630$ $m_2 = 0{\cdot}052$
Gd(III)	$GdCl_3$	0·1*M* TEAP	2·16	SCE	21	7	
H(I)	HCl	0·1*M* TEAP	1·08	SCE	30	5	
H(I)	HCl	0·1*M* TEAP	−0·01(1) 0·17(2) 1·14(3)	SCE	?	23	$s_1 = 300$ $s_2 = 2260$; $n_2 = 1$ $s_3 = 2600$; $n_3 = 1{\cdot}04$
H(I)	$HClO_4$	0·1*M* TEAP	1·14	SCE	?	23	$s = 2000$; $n = 0{\cdot}95$
H(I)	$HClO_4$	0·1*M* TEAP	0·96	Ag/DMSO	?	35	$n = 0{\cdot}75$
H(I)	H_2SO_4	0·1*M* TEAP	1·12	SCE	?	23	$s = 2400$; $n = 0{\cdot}90$
H(I)	H_2SO_4	0·1*M* TEAP	1·06	SCE	30	5	
H(I)	$HC_2H_3O_2$	0·1*M* TEAP	1·91(1) 2·22(2)	SCE	?	23	$s_1 = 200$ $s_2 = 1260$
H(I)	$HC_2H_3O_2$	0·1*M* TEAP	2·3	SCE	30		
HSO_4^-	TEA–HSO_4^-	0·1*M* TEAP	2·5	SCE	30	5	
Hf(IV)	$HfCl_4$	0·1*M* TEAP	0·98(1) 1·38(2)	SCE	25	32	$x_1 = -0{\cdot}054$ $x_2 = -0{\cdot}15$
Hf(IV)	$HfCl_4$	0·1*M* $TEANO_3$	1·07(1) 1·17(2)	SCE	21	1	
Ho(III)	$HoCl_3$	0·1*M* TEAP	2·09	SCE	21	7	$n = 3$
K(I)	KCl	0·1*M* TEAP	−0·01(1) 0·17(2) 2·22(3)	SCE	?	23	$s_1 = 200$ $s_2 = 2020$; $n_2 = 1$ $s_3 = 2320$; $n_3 = 0{\cdot}95$
K(I)	$KClO_4$	0·1*M* TEAP	2·11	SCE	?	23	$s = 2240$; $n = 0{\cdot}94$
K(I)	$KClO_4$	0·1*M* TEAP	1·97	Ag/DMSO	?	35	$n = 0{\cdot}99$; $I = 1{\cdot}42$
K(I)	$KClO_4$	0·1*M* TBAP	2·362	Hg Pool	25	11	$m = 0{\cdot}060$
K(I)	$KClO_4$	0·1*M* TBAP	2·06	SCE	25	9	
K(I)	$KClO_4$	0·1*M* $TEANO_3$	2·11	SCE	21	1	

TABLE 1 (*Continued*)

Active species	Form used	Inert electrolyte	$-E_{1/2}$, V	Reference electrode	T, °C	Ref.	Miscellaneous
K(I)	?	0·1M TBAP	2·070	SCE	25	11	m = 0·062; D = 6·69
La(III)	$LaCl_3$	0·1M TEAP	2·26	SCE	21	7	n = 3
Li(I)	LiCl	0·1M $TEANO_3$	2·45	SCE	21	1	
Li(I)	$LiClO_4$	0·1M TEAP	2·38	Ag/DMSO	?	35	n = 0·73; I = 1·61
Li(I)	$LiNO_3$	0·1M TBAP	2·38	SCE	25	9	
Mg(II)	$Mg(ClO_4)_2$	0·1M TEAP	2·44	Ag/DMSO	?	35	n = 2·22
Mg(II)	$Mg(ClO_4)_2$	0·1M $TEANO_3$	2·28	SCE	21	1	
Mg(II)	$Mg(NO_3)_2$	0·1M TBAP	2·19	SCE	25	9	
Mn(II)	$Mn(ClO_4)_2$	1·0M $KClO_4$	1·683	SCE	25	11	m = 0·040; D = 2·90
Mn(II)	$Mn(ClO_4)_2$	1·0M $KClO_4$	1·643	SCE	35	11	m = 0·034
Mn(II)	$Mn(ClO_4)_2$	1·0M $KClO_4$	1·810	Hg Pool	25	11	m = 0·038
Mn(II)	$Mn(ClO_4)_2$	1·0M $KClO_4$	1·823	Hg Pool	35	11	m = 0·038; D = 3·70
Mn(II)	$Mn(ClO_4)_2$	0·1M TEAP	1·57	Ag/DMSO	?	35	n = 1; I = 1·58
Mn(II)	$MnCl_2$	0·1M TBAP	1·73	SCE	25	9	
Na(I)	$NaClO_4$	0·1M $TEANO_3$	2·07	SCE	21	1	
Na(I)	$NaClO_4$	0·1M TEAP	1·96	Ag/DMSO	?	35	n = 0.96; I = 1·42
Na(I)	$NaHSO_4$	0·1M TEAP	2·07	SCE	30	5	
Nb(V)	$NbCl_5$	0·1M $TEANO_3$	0·92	SCE	21	1	
Nd(III)	$NdCl_3$	0·1M TEAP	2·20	SCE	21	7	n = 3
NH_3	NH_3	0·1M TEAP	−0·02	SCE	?	23	s = 475
NH_4(I)	NH_4Cl	0·1M TEAP	0·17(1) 2·04(2)	SCE	?	23	n_1 = 1; s_1 = 1560 n_2 = 1; s_2 = 1280
Ni(II)	$Ni(ClO_4)_2$	0·1M TBAP	1·322	Hg Pool	25	11	m = 0·053; D = 5·86
Ni(II)	$Ni(ClO_4)_2$	0·1M TBAP	1·207	Hg Pool	35	11	m = 0·053; D = 7·74
Ni(II)	$Ni(ClO_4)_2$	0·1M TEAP	0·95	Ag/DMSO	?	35	I = 1·71
Ni(II)	$Ni(ClO_4)_2$	0·1M $KClO_4$	1·124	Hg Pool	25	11	m = 0·067; D = 3·88
Ni(II)	$Ni(ClO_4)_2$	0·1M $KClO_4$	1·120	Hg Pool	35	11	m = 0·074; D = 5·66
Ni(II)	$Ni(NO_3)_2$	0·1M $KClO_4$	1·10	SCE	25	8	
Ni(II)	$Ni(ClO_4)_2$	1·0M $KClO_4$	1·155	Hg Pool	25	11	m = 0·091
Ni(II)	$Ni(ClO_4)_2$	1·0M $KClO_4$	1·122	Hg Pool	35	11	m = 0·085; D = 2·06
Ni(II)	$Ni(ClO_4)_2$	1·0M $KClO_4$	1·144	SCE	25	11	m = 0·107; D = 0·845
Ni(II)	$Ni(ClO_4)_2$	1·0M $KClO_4$	1·110	SCE	35	11	m = 0·087
Pb(II)	$Pb(ClO_4)_2$	0·1M TBAP	0·814	Hg Pool	25	11	m = 0·030
Pb(II)	$Pb(ClO_4)_2$	0·1M TEAP	0·43	Ag/DMSO	?	35	n = 1·99; I = 2·33
Pb(II)	$Pb(ClO_4)_2$	0·1M $KClO_4$	0·610	Hg Pool	25	11	m = 0·046; D = 2·25

Pb(II)	Pb(ClO$_4$)$_2$	0·1*M* KClO$_4$	0·651	Hg Pool	35	11	$m = 0{\cdot}052$; $D = 2{\cdot}61$
Pb(II)	Pb(ClO$_4$)$_2$	0·1*M* KClO$_4$	0·531	SCE	25	11	$m = 0{\cdot}030$
Pb(II)	Pb(ClO$_4$)$_2$	0·1*M* KClO$_4$	0·50	SCE	25	9	
Pb(II)	Pb(ClO$_4$)$_2$	1·0*M* KClO$_4$	0·541	SCE	25	11	$m = 0{\cdot}034$; $D = 1{\cdot}60$
Pb(II)	Pb(ClO$_4$)$_2$	1·0*M* KClO$_4$	0·537	SCE	35	11	$m = 0{\cdot}060$
Pb(II)	Pb(ClO$_4$)$_2$	1·0*M* KClO$_4$	0·561	Hg Pool	25	11	$m = 0{\cdot}048$
Pb(II)	Pb(ClO$_4$)$_2$	1·0*M* KClO$_4$	0·607	Hg Pool	35	11	$m = 0{\cdot}055$; $D = 2{\cdot}19$
Pr(III)	PrCl$_3$	0·1*M* TEAP	2·20	SCE	21	7	$n = 3$
Rb(I)	RbCl	0·1*M* TEANO$_3$	2·06	SCE	21	1	
Sb(III)	SbI$_3$	0·1*M* TEANO$_3$	0·36(1) 0·52(2) 1·13(3)	SCE	21	1	
Si(IV)	SiCl$_4$	0·1*M* TEANO$_3$	0·52(1) 1·09(2)	SCE	21	1	
Sm(III)	SmCl$_3$	0·1*M* TEAP	2·02(1) 2·12(2)	SCE	21	7	$n_1 = 1$ $n_2 = 2$
Sr(II)	Sr(NO$_3$)$_2$	0·1*M* TEANO$_3$	2·10	SCE	21	1	
Sr(II)	Sr(ClO$_4$)$_2$	0·1*M* TEAP	2·20	Ag/DMSO	?	35	$n = 2{\cdot}09$; $I = 2{\cdot}03$
Tb(III)	TbCl$_3$	0·1*M* TEAP	2·19	SCE	21	7	$n = 3$
Th(IV)	Th(ClO$_4$)$_4$	0·1*M* TEAP	1·55(1) 2·00(2)	Ag/DMSO	?	35	$n_1 = 0{\cdot}22$; $I = 0{\cdot}68$ $n_2 = 0{\cdot}41$; $I = 1{\cdot}58$
Th(IV)	Th(ClO$_4$)$_4$	0·1*M* TEAP	1·75(1) 2·14(2)	SCE	21	17	
Th(IV)	ThCl$_4$	0·1*M* TEAP	1·57(1) 1·72 to 1·95(2) 2·07(3)	SCE	21	17	
Th(IV)	Th(NO$_3$)$_4$	0·1*M* TEAP	1·57	SCE	21	17	
Ti(IV)	Et$_2$TiCl$_2$	0·1*M* TEANO$_3$	1·21	SCE	21	1	
Tl(I)	TlNO$_3$	0·1*M* TBAP	0·50	SCE	25	9	
U(IV)	UCl$_4$	0·1*M* TEAP	1·09(1) 1·56(2)	SCE	21	16	$x_1 = 0{\cdot}09$; $n_1 = 1$ $x_2 = 0{\cdot}22$; $n_2 = 3$
U(VI)	UO$_2$(NO$_3$)$_2$	0·1*M* TEAP	0·53	SCE	21	16	$x = 0{\cdot}056$; $n = 1$
Yb(III)	YbCl$_3$	0·1*M* TEAP	1·48(1) 2·21(2)	SCE	21	7	$n_1 = 1$ $n_2 = 2$
Zn(II)	Zn(ClO$_4$)$_2$	0·1*M* TEAP	0·95	Ag/DMSO	?	35	$n = 1{\cdot}80$; $I = 1{\cdot}94$
Zn(II)	Zn(ClO$_4$)$_2$	0·1*M* TBAP	1·322	Hg Pool	25	11	$m = 0{\cdot}029$; $D = 3{\cdot}38$
Zn(II)	Zn(ClO$_4$)$_2$	0·1*M* TBAP	1·298	Hg Pool	35	11	$m = 0{\cdot}036$; $D = 3{\cdot}58$
Zn(II)	Zn(ClO$_4$)$_2$	0·1*M* KClO$_4$	1·054	Hg Pool	25	11	$m = 0{\cdot}034$; $D = 5{\cdot}38$

TABLE 1 (*Continued*)

Active species	Form used	Inert electrolyte	$-E_{1/2}$, V	Reference electrode	T, °C	Ref.	Miscellaneous
Zn(II)	$Zn(ClO_4)_2$	1·0*M* $KClO_4$	1·089	Hg Pool	25	11	$m = 0{\cdot}108$
Zn(II)	$Zn(ClO_4)_2$	1·0*M* $KClO_4$	1·082	Hg Pool	35	11	$m = 0{\cdot}067$; $D = 3{\cdot}18$
Zn(II)	$Zn(ClO_4)_2$	1·0*M* $KClO_4$	1·099	SCE	25	11	$m = 0{\cdot}097$; $D = 2{\cdot}34$
Zn(II)	$Zn(ClO_4)_2$	0·1*M* $KClO_4$	1·066	SCE	35	11	$m = 0{\cdot}068$
Zr(IV)	$ZrCl_4$	0·1*M* $TEANO_3$	1·04	SCE	21	1	
Zr(IV)	$ZrCl_4$	0·1*M* TEAP	0·95(1) 1·38(2)	SCE	25	32	$x_1 = -0{\cdot}054$ $x_2 = -0{\cdot}15$
Zr(IV)	$ZrOCl_2$	0·1*M* TEAP	0·98(1) 1·38(2) 1·61(3)	SCE	25	32	$x_1 = -0{\cdot}86$ $x_2 = -0{\cdot}10$ $x_3 = -0{\cdot}14$
Zr(IV)	$ZrO(ClO_4)_2$	0·1*M* TEAP	0·95(1) 1·15(2) 2·05(3)	Ag/DMSO	?	35	$n_1 = 0{\cdot}57$ $n_2 = 0{\cdot}21$ $n_3 = 0{\cdot}40$

B. Organic Materials

Active species	Inert electrolyte	$-E_{1/2}$, V	Reference electrode	T, °C	Ref.	Miscellaneous
Al acetylacetonate	0·1*M* TEAP	2·2(1) 2·4(2)	SCE	25	14	
2-Aminoethanethiol	0·1*M* TEAP	0·17(1) 1·90(2) 2·40(3)	SCE	?	23	$n_1 = 2$; $s_1 = 4380$ $n_2 = 0{\cdot}95$; $s_2 = 2{\cdot}30$ $n_3 = 1$; $s_3 = 2280$
2-Aminoethanol	0·1*M* TEAP	$-0{\cdot}07(1)$ $-0{\cdot}02(2)$	SCE	?	23	$n_1 + n_2 = 2{\cdot}10$ $s_1 = 2120$; $s_2 = 1100$
4-Aminophenylsulphone	0·1*M* TEAP	0·17(1) 2·24(2)	SCE	?	23	$s_1 = 69$ $s_2 = 75$
Anthraquinone	0·5*M* LiCl	0·33(1) 0·70(2)	Hg Pool	?	8	
Asparagine	0·1*M* TEAP	2·382	SCE	25	52	$n = 0{\cdot}64$; $s = 4980$
Aspartic acid	0·1*M* TEAP	2·141(1) 2·618(2)	SCE	25	52	$n_1 = 0{\cdot}77$; $s_1 = 6120$ $n_2 = 0{\cdot}72$; $s_2 = 8660$
Butylamine	0·1*M* TEAP	0·00	SCE	?	23	$n = 1{\cdot}80$; $s = 3500$

Cysteine·HCl	0·1*M* TEAP	0·17(1) 1·38(2) 1·83(3) 2·07(4) 2·14(5)	SCE	?	23	$n_1 = 2{\cdot}11;\ s_1 = 4320$ $n_2 = 0{\cdot}10;\ s_2 = 900$ $n_3 = 0{\cdot}10;\ s_3 = 960$ $n_4 + n_5 = 1;\ s_4 = 900$ $s_5 = 1350$
Cysteine·HCl	0·1*M* TEAP	0·168(1) 1·321(2) 1·788(3) 2·014(4) 2·660(5)	SCE	25	52	$n_1 = 1{\cdot}62;\ s_1 = 18780$ $n_2 = 0{\cdot}69;\ s_2 = 4850$ $n_3 = 1{\cdot}02;\ s_3 = 3430$ $n_4 = 1{\cdot}12;\ s_4 = 9940$ $n_5 = 1{\cdot}10;\ s_5 = 6950$
Cystine·2HCl	0·1*M* TEAP	0·00(1) 0·17(2) 0·90(3) 1·44(4) 2·10(5)	SCE	?	23	$s_1 = 720$ $n_2 = 1{\cdot}82;\ s_2 = 3570$ $n_3 + n_4 = 1{\cdot}25$ $s_3 = 630;\ s_4 = 1890$ $n_5 = 1;\ s_5 = 3000$
Diethyl disulphide	0·1*M* TEAP	1·77(1) 2·04(2)	SCE	?	23	$n_1 = 0{\cdot}91;\ s_1 = 2840$ $n_2 = 1{\cdot}01;\ s_2 = 2310$
Diethyl sulphide	0·1*M* TEAP	No wave	SCE	?	23	
Dihydroxyphenylalanine	0·1*M* TEAP	2·375(1) 2·625(2)	SCE	25	52	$n_1 = 1{\cdot}23;\ s_1 = 4880$ $n_2 = 0{\cdot}90;\ s_2 = 5780$
Dimethyl sulphide	0·1*M* TEAP	No wave	SCE	?	23	
2,2′-Dithiobis(ethylamine)·2HCl	0·1*M* TEAP	0·00(1) 0·17(2) 0·97(3) 1·32(4) 1·96(5) 2·37(6)	SCE	?	23	$s_1 = 630$ $n_2 = 1{\cdot}89;\ s_2 = 3750$ $n_3 = 1{\cdot}06;\ s_3 = 2160$ $n_4 = 0{\cdot}31;\ s_4 = 1470$ $n_5 = 0{\cdot}30;\ s_5 = 1200$ $n_6 = 1;\ s_6 = 2000$
Ethanethiol	0·1*M* TEAP	0·17	SCE	?	23	$n = 1;\ s = 2850$
Ethanol	0·1*M* TEAP	No wave	SCE	?	23	
Glutamic acid	0·1*M* TEAP	2·123(1) 2·604(2)	SCE	25	52	$n_1 = 0{\cdot}91;\ s_1 = 5450$ $n_2 = 1;\ s_2 = 4140$
Glutamine	0·1*M* TEAP	2·090(1) 2·428(2)	SCE	25	52	$n_1 + n_2 = 0{\cdot}88$ $s_1 = 2870;\ s_2 = 2720$
Hydroxyproline	0·1*M* TEAP	2·317	SCE	25	52	$n = 0{\cdot}90;\ s = 6290$
Isoleucine	0·1*M* TEAP	2·465	SCE	25	52	$n = 0{\cdot}65;\ s = 4250$
Methionine	0·1*M* TEAP	2·435	SCE	25	52	$n = 1{\cdot}09;\ s = 6150$
p-Nitroanisole	0·5*M* LiCl	1·05(1) 1·35(2)	Hg Pool	?	10	

TABLE 1 (*Continued*)

Active species	Inert electrolyte	$-E_{1/2}$, V	Reference electrode	T, °C	Ref.	Miscellaneous
p-Nitrobenzaldehyde	0·5*M* LiCl	0·70(1) 0·90(2)	Hg Pool	?	10	
Nitrobenzene	0·5*M* LiCl	0·56(1) 1·0(2)	Hg Pool	?	8	
m-Nitrobenzoic acid	0·5*M* LiCl	0·29(1) 0·59(2) 0·87(3)	Hg Pool	25	8	
o-Nitrobenzoic acid	0·5*M* LiCl	0·29(1) 0·70(2)	Hg Pool	25	8	
p-Nitrobenzoic acid	0·5*M* LiCl	0·65(1) 0·90(2) 1·15(3)	Hg Pool	?	10	
m-Nitrophenol	0·5*M* LiCl	0·95(1) 1·15(2) 1·35(3) 1·45(4)	Hg Pool	?	10	
o-Nitrophenol	0·5*M* LiCl	0·37(1) 0·87(2)	Hg Pool	25	8	
p-Nitrophenol	0·5*M* LiCl	1·05(1) 1·5(2)	Hg Pool	?	10	
3-Nitrophthalic acid	0·5*M* LiCl	0·7(1) 1·1(2)	Hg Pool	?	10	
Nitroresorcinol	0·5*M* LiCl	0·37(1) 0·97(2)	Hg Pool	25	8	
Nitroterephthalic acid	0·5*M* LiCl	0·7(1) 1·1(2)	Hg Pool	?	10	
Oxalic acid	0·5*M* LiCl	0·84	Hg Pool	25	8	
Phenylalanine	0·1*M* TEAP	2·398	SCE	25	52	$n = 0{\cdot}93$; $s = 5550$
Proline	0·1*M* TEAP	2·307	SCE	25	52	$n = 1{\cdot}03$; $s = 8810$
p-Quinone	0·5*M* LiCl	0·02(1) 0·28(2)	Hg Pool	25	8	
Sodium *m*-nitrobenzoate	0·5*M* LiCl	0·95(1) 1·25(2)	Hg Pool	?	10	
Sodium *p*-nitrophenolate	0·5*M* LiCl	1·5	Hg Pool	?	10	

Tetraethylammonium chloride	0.1*M* TEAP	0.00(1) 0.17(2)	SCE	?	23	$s_1 = 180$ $s_2 = 2250$
Tetraethylammonium bisulphate	0·5*M* TEAP	2·5	SCE	30	5	
Threonine	0·1*M* TEAP	2·368	SCE	25	52	$n = 1{\cdot}07$; $s = 6600$
Tryptophan	0·1*M* TEAP	2·388	SCE	25	52	$n = 1{\cdot}02$; $s = 6180$
Tyrosine	0·1*M* TEAP	2·379	SCE	25	52	$n = 1{\cdot}07$; $s = 4990$

C. Gases

Active species	Inert electrolyte	$-E_{1/2}$, *V*	Reference electrode	*T*, °*C*	Ref.	Miscellaneous
NO	?	1·44	SCE	25	19	
N_2O_3	?	1·18	SCE	25	19	
NO_2	?	1·06(1) 1·53(2)	SCE	25	19	
N_2O	?	2·22	SCE	25	19	
O_2	0·1*M* $KClO_4$	0·586(1) 1·308(2)	SCE	25	11	$m_1 = 0{\cdot}112$ $m_2 = 0{\cdot}086$
O_2	0·1*M* TEAP	0·85(1) 2·20(2)	SCE	?	20	
O_2	0·1*M* TEAP	0·65(1) 1·70(2)	Ag/DMSO	?	35	
O_2	0·1*M* TBAP	0·77	SCE	?	6	
O_2	0·1*M* TBAP	0·777	SCE	25	11	$m = 0{\cdot}075$
O_2	0·1*M* TBAP	1·156	Hg Pool	25	11	$m = 0{\cdot}069$

Key to Table I

n = number of electrons transferred in the half-cell
D = diffusion coefficient in 10^6 cm²/sec.
m = slope of a plot of $E_{d,c}$ *vs.* $\log \dfrac{i}{i_d - i}$

I = diffusion-current constant = $i_d/Cm^{2/3}t^{1/6}$
s = i_d/concentration
$x = E_{3/4} - E_{1/4}$.

TEAP = tetraethylammonium perchlorate
Ag/DMSO = Ag/$AgCl_2^-$ reference in DMSO
$TEANO_3$ = tetraethylammonium nitrate

TBAP = tetrabutylammonium perchlorate
SCE = saturated calomel electrode (aqueous)
Hg Pool = mercury pool reference electrode

The figures in brackets after the $E_{1/2}$ values indicate the number of the wave.

ions they determined the diffusion potential between an aqueous SCE and a DMSO test solution.[2]

Iwamoto[3] investigated the electro-oxidation of iodide. Chronopotentiometric studies at a platinum-foil electrode indicated a two-step oxidation.

$$6I^- \rightarrow 2I_3^- + 4e^-$$

$$2I_3^- \rightarrow 3I_2 + 2e^-$$

This is in contrast to the oxidation of iodide ion in water, which proceeds by a single step.

Gutmann *et al.*[4] extended their previous studies to several silicon compounds, including $SiCl_4$, SiF_4, and compounds of the type RCl_3Si. The polarographic waves for the RCl_3Si species in DMSO occurred at approximately the same potential, permitting polarographic analysis for organic silicon.

Kolthoff and Reddy[5] studied the polarographic behavior of several acids and of cobalt and nickel in DMSO. They reported the polarization limits with sodium perchlorate and tetraethylammonium perchlorate supporting electrolytes, using the rotating platinum electrode (RPE), the rotating mercury pool electrode (RMPE), and the dropping mercury electrode (DME). These polarization limits are presented in Table II.

The polarographic characteristics of perchloric acid, sulphuric acid, hydrochloric acid, acetic acid, sodium bisulphate and tetraethylammonium bisulphate are included in Table I. Well-defined and identical current–voltage curves were observed for solutions of perchloric, hydrochloric, and sulphuric acids in $0{\cdot}1M$ sodium perchlorate; the half-wave potential was $-0{\cdot}67 \pm 0{\cdot}02$ V. The basic strength of DMSO is reported to be about the same as that of water. Because these acids gave the same polarographic wave, Kolthoff and Reddy concluded that sulphuric (K_1), perchloric, and hydrochloric acids are completely dissociated in DMSO. Amperometric titrations of dilute strong acid solutions can be carried out in DMSO; the current is measured at an applied potential of $-1{\cdot}00$ V.

Kolthoff and Reddy calculated from polarographic data the diffusion coefficient of the hydrogen ion in DMSO solutions of strong acids and found it to be $4{\cdot}4 \times 10^{-6}$ cm^2/sec at 30°. On the basis of the specific conductance calculated from these data, the proton-diffusion mechanism in DMSO was shown to be different from that in water.

Cobalt(II) and nickel(II) in $0{\cdot}1M$ sodium perchlorate gave sharp maxima, even in very dilute solution; no surface-active substance could be found which would entirely eliminate these maxima. Studies at the RMPE (120 rpm) gave well-defined waves without maxima. A dilute solution of sodium perchlorate in $0{\cdot}1M$ tetraethylammonium perchlorate (TEAP) gave a well-defined, nearly reversible wave for sodium with a half-wave potential of $-2{\cdot}07$ V.

In $0{\cdot}1M$ TEAP, quinhydrone and benzoquinone showed two cathodic waves of unequal height. The first wave was a one-electron reversible reduction, and the second wave was irreversible. When $0{\cdot}01M$ hydrochloric acid, acetic acid, or water was added, the second wave was shifted to more positive potentials until only one wave with a maximum was observed. This wave had a height equal to the sum of the heights of the original waves. Duroquinone gave two waves, the first reversible, the second irreversible. Tetrachloroquinone gave two irreversible waves of equal height. The authors

TABLE II.—POLARIZATION LIMITS IN DMSO

Supporting electrolyte	Electrode	Anodic limit, *V*	Cathodic limit, *V*	Reference electrode	E_{ecm}, *V*	Ref.
0·1*M* TBABr	RPE + RGE	+1·08	−2·8	Ag/DMSO		28
0·1*M* $TBAClO_4$	DME	+0·60	−3·00	Hg Pool	−0·058	11
0·1*M* $TBAClO_4$	DME	+0·20	−3·00	SCE		11
0·1*M* $TBAClO_4$	DME	+0·37	−2·70	SCE		10
0·1*M* $TBAClO_4$	DME	−0·41	−2·85	SCE		10
0·1*M* TBAI	DME	0·00	−2·40	Hg Pool	−0·10	11
0·1*M* $TEAClO_4$	DME	+0·25	−2·80	SCE		5
0·1*M* $TEAClO_4$	RPE	+0·70	−1·85	SCE		5
0·1*M* $TEAClO_4$	RPE + RGE	+1·73	−2·7	Ag/DMSO		28
0·1*M* $TEANO_3$	DME	−0·20	−2·74	SCE		4
0·1*M* TMACl	RPE + RGE	+1·15	−2·8	Ag/DMSO		28
0·1*M* KBF_4	RPE + RGE	+1·73	−2·70	Ag/DMSO		28
0·1*M* $KClO_4$	DME	+0·50	−1·81	Hg Pool	−0·22	11
0·1*M* $KClO_4$	DME	+0·20	−1·84	SCE		11
0·1*M* $KClO_4$	DME	+0·30	−1·88	SCE		10
0·1*M* $KClO_4$	RPE + RGE	+1·73	−2·70	Ag/DMSO		28
0·1*M* $KClO_4$–0·1*M* H_2O	DME	+0·40	−1·81	Hg Pool	−0·16	11
1*M* $KClO_4$	DME	+0·20	−1·84	SCE	−0·28	11
0·1*M* KI	DME	+0·10	−1·40	Hg Pool	−0·08	11
0·1*M* KI–0·1*M* H_2O	DME	0·00	−1·40	Hg Pool	−0·15	11
0·1*M* KNO_3	RPE + RGE	+1·73	−2·70	Ag/DMSO		28
0·1*M* $K_2S_2O_8$	RPE + RGE	+1·73	−2·70	Ag/DMSO		28
0·1*M* LiCl	RPE + RGE	+1·15	−3·05	Ag/DMSO		28
0·1*M* LiCl	DME	−0·21	−2·77	SCE		10
0·1*M* $LiClO_4$	RPE + RGE	+1·73	−3·05	Ag/DMSO		28
0·01*M* $NaC_2H_3O_2$	DME	−0·10	−1·96	SCE		10
0·1*M* $NaClO_4$	DME	+0·25	−1·90	SCE		5
0·1*M* $NaClO_4$	RPE	+0·70	−1·85	SCE		5
0·1*M* $NaClO_4$	RMPE	+0·3	−1·9	SCE		5
0·1*M* $NaClO_4$	RPE + RGE	+1·73	−2·45	Ag/DMSO		28
0·1*M* $NaNO_3$	DME	+0·31	−1·85	SCE		10

Key to Table II

DME = dropping mercury electrode.
RPE = rotating platinum electrode
RGE = rotating graphite electrode
SCE = saturated calomel electrode (aqueous)
Hg Pool = mercury pool reference electrode

RMPE = rotating mercury pool electrode.
Ag/DMSO = $Ag/AgCl_2^-$ electrode in DMSO
TBA = tetrabutylammonium salt
TEA = tetraethylammonium salt
TMA = tetramethylammonium salt

concluded that the polarographic behavior of quinones in DMSO provided evidence that DMSO is a much weaker acid than water. In relatively acidic solvents such as water or acetic acid, the general reduction mechanism for the two-electron reduction of organic compounds at the DME was reported to be:

$$R + e^- \rightarrow R\cdot^-$$

$$R\cdot^- + HS \rightarrow RH\cdot + S^-$$

$$RH\cdot + e^- \rightarrow RH^-$$

$$RH^- + HS \rightarrow RH_2 + S^-$$

Since the electron affinity of RH· has been shown always to be greater than that of R, the two are reduced at the same potential in a single two-electron reduction wave, such as is observed for quinones in water. In DMSO, as well as in dimethylformamide and acetonitrile (all weakly acidic), the reduction mechanism for quinones was reported to be:

$$R + e^- \rightarrow R\cdot^- \text{ (first wave)}$$

$$R\cdot^- + e^- \rightarrow R^{2-} \text{ (second wave)}$$

R^{2-} diffuses into solution, where:

$$R^{2-} + HS \rightarrow RH^- + S^- \text{ (slow)}$$

$$RH^- + HS \rightarrow RH_2 + S^- \text{ (slow)}$$

A double wave results since $R\cdot^-$ is reduced at a more negative potential than R. The second wave is somewhat smaller, probably because of limited protonation of $R\cdot^-$ or repulsion of $R\cdot^-$ by the negatively-charged mercury drop. When a proton donor is added, it reacts with R^{2-} but not with $R\cdot^-$, and the rate of the reaction

$$R^{2-} + HA \rightarrow RH^- + A^-$$

becomes potential-determining. The second wave, therefore, shifts toward the first, and eventually merges with it.

Oxygen gave two waves in DMSO, although only one drawn-out wave with a maximum was observed in concentrated solutions. Also, only one wave was observed in 0·1*M* sulphuric acid and in a 0·1*M* ammonium acetate and 0·1*M* acetic acid buffer. The polarography of oxygen showed qualitatively the same effects observed with quinones, but more detailed studies were considered necessary. Peover and White[6,7] studied the reduction of oxygen to superoxide ion by a.c. and d.c. polarography. Their results, included in Table I, showed that the reduction is diffusion-controlled, and that the superoxide ion has considerable stability in DMSO. The reduction is reversible. On addition of a strong acid, the process reverts to the normal two-electron reduction.

The preparative-scale reduction of oxygen to superoxide ion was studied by Maricle and Hodgson.[8] Their polarographic work was similar to that of Peover and White. Preparative-scale reductions produced both tetrabutylammonium superoxide and potassium superoxide. The polarographic reduction of oxygen in DMSO that was 0·1*M* in TEAP was studied by Johnson *et al.*[9] As shown in Table I, two waves were obtained; in agreement with other workers, the authors found that the first wave was due to the reduction of oxygen to superoxide ion. The second wave, studied as a function of various cations at varying concentrations, was attributed to the combination of superoxide with one electron plus a cation to give a peroxide product.

Jones and Fritsche[10] used potential-sweep chronoamperometry at a hanging mercury drop electrode to study DMSO as an electrochemical solvent, and reported working ranges for various supporting electrolytes. The behaviour of oxygen differs from that reported by Johnson *et al.*,[9] indicating, as the latter authors mentioned, that the reduction of oxygen in DMSO is very dependent on the nature and concentration of the supporting electrolyte. Cadmium and magnesium were also studied.

In 1962, Burras[11] carried out an extensive study into the polarographic behaviour of a number of common cations in DMSO. The effects of various parameters were also investigated. Burras employed both aqueous saturated calomel and mercury-pool reference electrodes, and used a variety of supporting electrolytes. The potentials of the electrocapillary maxima, and the usable potential ranges, are reported in Table II. The effects of variation of temperature and of supporting electrolyte concentration were studied. Also, the influence of a maximum suppressor and of water on the polarogram of cadmium, and of added chloride on the cadmium and lead polarograms, was investigated. The polarographic data for the various ions studied by Burras are included in Table I.

Gutmann and Schöber[12] studied the polarographic behaviour of various chromium(III)–anion systems. The equilibria of various co-ordination forms of chromium(III) with chloride ion and DMSO were investigated. The co-ordination forms $[Cr(DMSO)_6]^{3+}$, $[CrCl_2(DMSO)_4]^+$, $[CrCl_3(DMSO)_3]$, $[CrCl_4]^-$, $[CrCl_5]^{2-}$, and $[CrCl_6]^{3-}$ were observed. Schöber and Rahak[13] discussed the application, to non-aqueous solutions, of methods used to establish reversibility in aqueous solution. The Cr(III)–Cr(II) redox system in DMSO was investigated for reversibility. Within the limits of error of the experiment, both chromic nitrate and $CrCl_4^-$ were found to be entirely reversibly reduced in this solvent.

Dehn *et al.*[14] studied the polarographic behaviour of aluminium chloride and aluminium acetylacetonate in DMSO. One wave was reported for the former, two for the latter; half-wave potentials are shown in Table I. The authors suggested that since aluminium can be extracted as the acetylacetonate, the polarographic method would be useful as an analytical tool for aluminium.

The lanthanides (as chlorides) were investigated polarographically by Gritzner *et al.*[15] Lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium, dysprosium, holmium, and erbium gave one wave; samarium, europium, and ytterbium gave two waves. All waves were diffusion-controlled and had no maxima.

The polarographic behaviour of uranium compounds in DMSO was studied by Michlmayr *et al.*[16] Uranium tetrachloride shows two waves, the first involving one electron, the other three electrons. Both waves are quite irreversible and the second wave exhibits a maximum. However, both waves were found to be diffusion-controlled. Uranyl compounds exhibit one diffusion-controlled, well-defined wave involving the one-electron reduction to UO_2^+. The effect of added water on the waves was also reported.

Gritzner *et al.*[17] investigated the polarography of thorium salts in DMSO. Thorium tetrachloride gives three waves at a concentrations below millimolar; at higher concentrations, the third wave merges with the most cathodic wave. Thorium tetraperchlorate monohydrate and trihydrate give two waves, whereas thorium tetranitrate pentahydrate and thorium tetranitrate solvated with four DMSO molecules give only one wave.

DMSO solutions of sodium chloride and sodium iodide were subjected to electrolysis at platinum electrodes.[18] The cathode reaction involved initial discharge of sodium ions, after which the sodium metal reacted with the solvent. An anodic reaction was also reported that involved reactions of the iodide and tri-iodide ions.

Gritzner *et al.*[19] found that nitrogen monoxide, dioxide and trioxide, and nitrous oxide could be determined polarographically in DMSO. Lindbeck and Young[20] investigated the polarographic and controlled-potential coulometric determination of the nitric acid oxidation products of soil humic acid. Reduction waves were found which compared closely with the polarographic reduction waves of the nitrobenzoic acids. Although the authors discussed the advantages of the extended potential range of DMSO, their choice of a $0{\cdot}1M$ sodium hydroxide supporting electrolyte precluded the possibility of using it, by limiting the range to about that of water. Lindbeck and Freund[21] studied substituted nitrobenzene compounds in DMSO by polarography and controlled-potential coulometry. The main purpose of their paper was to report n values for the nitrobenzene compounds. Polarography was used only to determine the proper potentials for use in constant-potential coulometry.

Di Giacomo *et al.*[22] reported that phenylfluorone in DMSO gives two waves, as opposed to one in water. The second wave is higher than the first, and can be resolved by linear-sweep polarography into two steps; the more cathodic step shows kinetic characteristics. In the presence of benzoic acid, the two reduction waves are of equal height. A reduction mechanism is proposed.

A number of sulphydryl, disulphide, amine compounds, and sulphur-amino acids were studied polarographically in DMSO by Giang *et al.*[23] The half-wave potentials, n values, and i_d/C values given are shown in Table I. The authors reported that all of the waves were diffusion controlled and irreversible. An excellent review of electrochemistry in DMSO was published in 1967 by Butler.[24] Both polarographic data and reference electrodes were discussed.

REFERENCE ELECTRODES

A reference electrode employing the silver–silver chloride couple in DMSO was constructed by Courtot-Coupez and Le Demezet.[25] The range of electroactivity in DMSO was tested, using a polished platinum electrode in the presence of sodium, potassium, lithium and quaternary ammonium perchlorates. Ranges varied from 4·18 to 4·80 V.

Smyrl[26] determined the standard cell potential of $Pt_{(s)}/Li_{(s)}/LiCl_{(soln)}/TlCl_{(s)}/Tl_{(Hg)},_{(l)}/Pt_{(s)}$ in DMSO. The standard potential for the analogous calcium amalgam electrode was estimated. McMaster and co-workers[27] developed and tested a reference electrode consisting of a saturated solution of $Zn(ClO_4)_2{\cdot}4DMSO$ in contact with a saturated zinc amalgam. By comparing their half-wave potentials with those reported by other workers, the potential of this reference electrode was found to be $-1{\cdot}10$ V *vs.* aqueous SCE. Relative reduction–potential scales for several solvents were established.

A reference electrode employing the Ag/$AgCl_2^-$ couple in DMSO was developed and tested by Courtot-Coupez and Le Demezet.[28] The regions of electroactivity of the platinized platinum, mercury, graphite and silver electrodes were determined, and are listed in Table II. A reference electrode of Ag/AgCl/LiCl in methanol was developed for potentiometric titrations in DMSO.[29] Rallo and Ceccaroni[30] described a reference electrode consisting of cadmium metal in contact with saturated DMSO solutions of $CdCl_2$, $CdCl_2 \cdot H_2O$, or NaCl. The electrode was considered suitable for use in electrochemical studies.

Synnott and Butler[31] developed and tested four chloride reference electrodes in DMSO. The half-cell Tl(Hg)/TlCl in DMSO appeared to be a good reference electrode for use in this solvent.

RECENT STUDIES

Polarographic investigations on DMSO solutions of zirconium and hafnium compounds were carried out by Michlmayr and Gutmann.[32] The half-wave potentials, the nature of the limiting currents, the temperature coefficients of half-wave potentials and wave heights, the reversibility or irreversibility of the electrode processes, and the influence of water were determined. Schmid and Gutmann[33] reported the half-wave potentials in DMSO (*vs.* aqueous SCE) of thallium(I), rubidium, potassium, sodium, barium, zinc, cadmium, manganese(II), cobalt(II), and nickel perchlorates. These potentials were referred to that of bis(biphenyl)chromium(I) iodide. Reduction mechanisms, various analytical aspects of the system, and the effects of water were discussed.

Pyatnitskii and Ruzhanskaya[34] reported half-wave potentials for the 8-hydroxyquinolinates of copper(II), lead, iron(III), cadmium, and bismuth in mixtures of methanol and DMSO, and with eleven other solvents. Lithium chloride was used as the supporting electrolyte. No correlation was found between the half-wave potential and the dielectric constant of the solvent. Kumar and Pantony[35] investigated the polarographic behaviour of a number of anhydrous inorganic perchlorates in DMSO. Gritzner *et al.*[36] applied oscillographic polarography to the study of DMSO solutions of the lanthanides. These results were compared with those of classical polarography. The peak potentials are shown in Table III.

Haynes and Sawyer[37] have employed chronopotentiometry, controlled-potential coulometry, gas chromatography, and pH titrations to investigate the electrochemical reduction of carbon dioxide in DMSO solutions at gold and mercury electrodes. At a gold electrode, irreversible but well-defined chronopotentiograms were observed; the reduction is a one-electron process and is diffusion-controlled. The diffusion-controlled reduction at a mercury electrode, complicated by equilibria involving water has $\alpha n = 0{\cdot}64$. Controlled-potential coulometry at a mercury electrode indicates an overall one-electron process. In anhydrous medium, the reduction products at both electrodes are carbon monoxide and carbonate ion; some bicarbonate and formate ions are formed in the presence of water.

Johnson *et al.*[38] observed a unique reduction wave, at potentials less cathodic than the reduction wave of either reducible species alone, in DMSO solutions containing both oxygen and one of the metal ions, cadmium, zinc, strontium, thallium(I), or yttrium. The variation of the height of this wave was studied as a function of concentration of oxygen and the various metal ions. Studies of this type revealed

TABLE III.—OSCILLOGRAPHIC PEAK POTENTIALS IN DMSO[36]

Species	$-E$ Reduction potential, V	$-E$ Oxidation potential, V
La(III)	2·39	2·31
Ce(III)	2·39	2·39
Pr(III)	2·39	2·30
Nd(III)	2·42	2·29
Sm(III)	2·11(1) 2·30(2)	2·05
Eu(III)	0·86(1) 2·28(2)	0·73(1) 2·11(2)
Gd(III)	2·42	2·36
Tb(III)	2·42	2·34
Dy(III)	2·42	2·33
Ho(III)	2·40	2·36
Er(III)	2·42	2·33
Yb(III)	2·39	2·20

the stoichiometry of the materials which caused the reduction wave. Controlled-potential coulometry was employed to determine values of n. Massive preparation of reduction products by controlled-potential electrolysis, along with the above information, revealed the probable reduction mechanism. In the cases of zinc, strontium, and thallium(I), the reduction was of metal ion plus oxygen to the superoxide; cadmium and yttrium with oxygen were reduced to the peroxides.

Fujinaga *et al.*[39] found that in DMSO containing between 10 and 30% water, the first oxygen wave (reduction to superoxide ion) becomes a two-electron wave, because of protonation by water. The polarographic diffusion coefficients of oxygen in the mixed solvent were calculated.

Pasadas *et al.*[40] studied the kinetics of hydrogen evolution on an iron electrode as a function of hydrochloric acid concentration; excess of potassium perchlorate was employed. Temperatures were varied from 20° to 45°. A two-step mechanism was proposed in which the simple discharge of solvated hydrogen ions was rate-determining.

The function of a hydrogen electrode in DMSO was studied by Courtot-Coupez and Le Demezet.[41] The authors determined the pK values of a number of acids, and reported the ion product of the solvent to be $pK_s = 33{\cdot}3 \pm 0{\cdot}05$. This differs greatly from the value reported by Reddy[42] ($pK_s = 17{\cdot}3$), but is in virtual agreement with the value determined spectrophotometrically by Steiner[43,44] ($pK_s = 32$).

Rallo *et al.*[45] studied the polarographic reduction of nitric oxide in 0·1*M* TEAP. Solutions with varying NO/N_2 content were investigated. One wave appeared when there was less than 10% NO in the gas mixture; with more than 10% NO, a second, more anodic wave appeared, which was not diffusion-controlled and was thought to be due to the reduction of a dimer. The rate-determining dimerization which preceded reduction was thought to control the wave height.

Michlmayr and Sawyer[46] investigated the electrochemical behaviour of the hydrogen halides at platinum electrodes in DMSO by chronopotentiometry, controlled-potential coulometry, and cyclic voltammetry. The results indicated that the oxidation products of the hydrogen halides reacted with the solvent. In the cases of HCl and

HBr, a catalytic process occurred which enhanced the value of $i\tau^{1/2}$ by a factor of 5–10.

The electrochemical oxidation of formate has been studied at gold and platinum electrodes, by chronopotentiometry, controlled-potential coulometry and cyclic voltammetry.[47] Well-defined chronopotentiograms were obtained, with quarter-wave potentials of 0·33 and —0·07 V *vs.* SCE at a gold and a platinum electrode respectively. The process is diffusion-controlled. The oxidation products were carbon dioxide and hydrogen ions, which react with formate ion. Thus, the overall reaction is a one-electron oxidation in which half a mole of carbon dioxide and half a mole of formic acid are formed for each mole of formate ion electrolysed.

Jacobson and Sawyer[48] studied the electrochemical oxidation of oxalate at a gold electrode. The chronopotentiometric quarter-wave potential was 1·25 V *vs.* SCE. The final oxidation product was carbon dioxide, but an unstable intermediate was formed during the oxidation process. In the absence of excess of hydroxide ion, oxalate ion is partially hydrolysed to the hydrogen oxalate ion, which is oxidized to carbon dioxide and hydrogen ions.

Buchta and Evans[49] examined the electrochemical behaviour of 1,3-diphenyl-1,3-propanedione, as well as a number of other β-diketones. Controlled-potential coulometry at the potential for the first wave gave an *n*-value of 0·55. The products were found to be the enolate of 1,3-diphenyl-1,3-propanedione and the pinacole 1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol. Further electrolysis resulted in an increase in current, followed by a decrease to the residual value. This was caused by an electrolytic autocatalytic decomposition of the pinacol in a base-catalysed reverse aldol condensation to benzil and acetophenone. The presence of the benzil radical anion was confirmed by ESR spectroscopy. Other β-diketones behaved in an analogous fashion.

Goolsby and Sawyer[50] studied the electrochemistry of hydroxylamine at gold and platinum electrodes in 0·2*M* lithium perchlorate in DMSO. The electroactive species, NH_2OH, is oxidized irreversibly in a diffusion-controlled, two-electron process. The chronopotentiometric $E_{1/4}$ values were —0·84 V *vs.* SCE at a platinum electrode and —1·18 V at a gold electrode. The major products are water, hydrogen ion and nitrous oxide. The rate-controlling step is a one-electron process which follows a preceding chemical reaction of a hydroxide ion with hydroxylamine.

The electrochemical oxidation, at platinum electrodes, of hydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine in DMSO was studied by Michlmayr and Sawyer.[51] In each case the oxidation involved one electron. Chronopotentiometric quarter-wave potentials were reported as 0·00, 0·02, and 0·03 V *vs.* SCE, for the three compounds in the order listed above. The oxidation products were identified and mechanisms proposed.

Koch and Purdy [52] studied the polarographic behaviour of amino-acids in DMSO. Nine amino-acids, asparagine, hydroxyproline, isoleucine, methionine, phenylalanine, proline, threonine, tryptophan, and tyrosine, gave single waves involving the one-electron reduction of the proton of the carboxyl group. Five amino-acids, dihydroxyphenylalanine, glutamic acid, aspartic acid, glutamine, and cysteine gave multiple waves.

The electrical double-layer in DMSO solutions was studied by Payne.[53] He noted a strong resemblance in electrocapillary curves and double-layer capacities of DMSO and aqueous solutions. Anions are specifically adsorbed from DMSO solutions in the order $I^- > Br^- > Cl^- > NO_3^- > ClO_4^- > PF_6^-$; cations are not significantly adsorbed. The electrocapillary maximum is shifted in the positive direction in DMSO as compared to water, and a large hump appears close to the limit of anodic polarization in solutions where the anion is not strongly adsorbed. The influence of diffusion-layer capacity is more marked in DMSO. The interfacial tension at the electrocapillary maximum is about 60 dyn/cm lower (370·5 dyn/cm) than in water.

Payne[54] reported the occurrence of capacity humps on the electrocapillary curve for 0·1*M* KPF_6 solutions in DMSO. The hump appears on the anodic side of the electrocapillary maximum.

Synnott and Butler[55] studied the equilibria of silver chloride in DMSO–water mixtures containing excess of chloride. They used potentiometric results to determine equilibrium constants for the system.

Gutmann[56] reviewed the effect of the donor properties of various solvents, including DMSO. Also discussed were the effects of the acceptor properties of metal ions, solvation of metal ions and complex formation on half-wave potentials and the thermodynamics of reduction processes.

Zusammenfassung—Es wird eine Übersicht über voltametrische Untersuchungen mit Dimethylsulfoxid als Trägerelektrolyt gegeben. Sie umfaßt Einzelheiten über die untersuchten anorganischen und organischen Systeme sowie über die für dieses Medium entwickelten Bezugselektroden.

Résumé—On présente une revue des études voltammétriques utilisant le diméthylsulfoxyde comme électrolyte-support, et celle comprend des détails de systèmes minéraux et organiques étudiés et des électrodes de référence élaborées pour l'emploi dans ce milieu.

REFERENCES

1. V. Gutmann and G. Schöber, *Z. Anal. Chem.*, 1959, **171**, 339.
2. G. Schöber and V. Gutmann, *Monatsh.*, 1959, **90**, 897.
3. R. T. Iwamoto, *Anal. Chem.*, 1959, **31**, 955.
4. G. Schöber, V. Gutmann and P. Heilmayer, *Monatsh.*, 1961, **92**, 240.
5. I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, 1961, **108**, 980.
6. M. E. Peover and B. S. White, *Chem. Commun.*, 1965, 183.
7. *Idem*, *Electrochim. Acta*, 1966, **11**, 1061.
8. D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, 1965, **37**, 1562.
9. E. L. Johnson, K. H. Pool and R. E. Hamm, *ibid.*, 1966, **38**, 183.
10. J. L. Jones and H. A. Fritsche, Jr., *J. Electroanal. Chem.*, 1966, **12**, 334.
11. R. T. Burras, *Ph.D. Dissertation*, University of Tennessee, 1962.
12. V. Gutmann and G. Schöber, *Monash.*, 1962, **93**, 212.
13. G. Schöber and G. Rahak, *ibid.*, 1962, **93**, 445.
14. H. Dehn, V. Gutmann and G. Schöber, *ibid.*, 1962, **93**, 453.
15. G. Gritzner, V. Gutmann and G. Schöber, *ibid.*, 1965, **96**, 1056.
16. M. Michlmayr, G. Gritzner and V. Gutmann, *Inorg. Nucl. Chem. Letters*, 1966, **2**, 227.
17. G. Gritzner, V. Gutmann and M. Michlmayr, *Z. Anal. Chem.*, 1967, **224**, 245.
18. M. C. Giordano, J. C. Bazan and A. J. Arvia, *Electrochim. Acta*, 1966, **11**, 741.
19. G. Gritzner, V. Gutmann and G. Schöber, *Mikrochim. Acta*, 1964, 193.
20. M. R. Lindbeck and J. L. Young, *Soil Sci.*, 1966, **101**, 366.
21. M. R. Lindbeck and H. Freund, *Anal. Chim. Acta*, 1966, **35**, 74.
22. F. DiGiacomo, F. Rallo and L. Rampazzo, *Ric. Sci.*, 1967, **37**, 1085.
23. B. Y. Giang, G. D. Christian and W. C. Purdy, *J. Polarographic Soc.*, 1967, **13**, 17.
24. J. N. Butler, *J. Electroanal. Chem.*, 1967, **14**, 89.
25. J. Courtot-Coupez and M. Le Demezet, *Compt. Rend., Ser. C*, 1966, **263**, 997.
26. W. H. Smyrl, *Diss. Abstr. B*, 1967, **28**, 637.

27. D. L. McMasters, R. B. Dunlap, J. R. Kuempel, L. W. Kreiger and T. R. Shearer, *Anal. Chem.*, 1967, **39**, 103.
28. J. Courtot-Coupez and M. Le Demezet, *Bull. Soc. Chem. France*, 1967, **39**, 888.
29. T. Jasinski and E. Kwiatkowski, *Zesz. Nauk. Mat. Fiz., Khim., Wyzsza Szk. Pedagog. Gnadsku*, 1968, **8**, 101.
30. F. Rallo and G. Ceccaroni, *Ric. Sci.*, 1968, **38**, 1067.
31. J. C. Synnott and J. N. Butler, *Anal. Chem.*, 1969, **41**, 1890.
32. M. Michlmayr and V. Gutmann, *Electrochim. Acta*, 1968, **13**, 1071.
33. R. Schmid and V. Gutmann, *Chem. Zvesti*, 1969, **23**, 746.
34. I. V. Pyatnitskii and P. Ruzhanskaya, *Zh. Analit. Khim.*, 1970, **25**, 1063.
35. G. P. Kumar and D. A. Pantony, *J. Polarographic Soc.*, 1968, **14**, 84.
36. G. Gritzner, V. Gutmann and R. Schmid, *Electrochim. Acta*, 1968, **13**, 919.
37. L. V. Haynes and D. T. Sawyer, *Anal. Chem.*, 1967, **39**, 332.
38. W. L. Johnson, K. H. Pool and R. E. Hamm, *ibid.*, 1967, **39**, 888.
39. T. Fujinaga, K. Izutsu and T. Adachi, *Bull. Chem. Soc. Japan*, 1969, **42**, 140.
40. D. Pasadas, J. J. Podesta and A. J. Arvia, *Electrochim. Acta*, 1970, **15**, 1225.
41. J. Courtot-Coupez and M. Le Demezet, *Compt. Rend., Ser. C*, 1968, **266**, 1438.
42. T. B. Reddy, *Ph.D. Dissertation*, University of Minnesota, 1960.
43. E. C. Steiner and J. D. Starkey, *J. Am. Chem. Soc.*, 1963, **85**, 3054.
44. E. C. Steiner, J. D. Starkey, J. M. Tralmer and R. O. Trucks, *Div. Petrol. Chem., Amer. Chem. Soc., Preprints*, 1967, **12**, C-11.
45. F. Rallo, L. Rampazzo and F. DiGiacomo, *Ric. Sci.*, 1969, **38**, 1085.
46. M. Michlmayr and D. T. Sawyer, *J. Electroanal. Chem.*, 1969, **23**, 387.
47. E. Jacobsen, J. L. Roberts and D. T. Sawyer, *ibid.*, 1968, **16**, 351.
48. E. Jacobsen and D. T. Sawyer, *ibid.*, 1968, **16**, 361.
49. R. C. Buchte and D. H. Evans, *Anal Chem.*, 1968, **40**, 2181.
50. C. D. Goolsby and D. T. Sawyer, *J. Electroanal. Chem.*, 1968, **19**, 405.
51. M. Michlmayr and D. T. Sawyer, *ibid.*, 1969, **23**, 375.
52. T. R. Koch and W. C. Purdy, *Anal. Chim. Acta*, 1971, **54**, 271.
53. R. Payne, *J. Am. Chem. Soc.*, 1967, **89**, 489.
54. *Idem. J. Phys. Chem.*, 1967, **71**, 1548.
55. J. C. Synnott and J. N. Butler, *ibid.*, 1969, **73**, 1470.
56. V. Gutmann, *Allg. Prakt. Chem.*, 1970, **21**, 116.

Talanta, 1972, Vol. 19, pp. 1009 to 1017. Pergamon Press. Printed in Northern Ireland

PRETREATED BRIGHT PALLADIUM ELECTRODE IN POTENTIOMETRIC REDOX TITRATIONS

TITRATION OF $Cr_2O_7^{2-}$ AND Ce^{4+} WITH Fe^{2+}

CANDIN LITEANU and IOVANCA HAIDUC
University of Cluj, Department of Analytical Chemistry, Cluj, Romania

(*Received* 2 *June* 1971. *Accepted* 5 *January* 1972)

Summary—The behaviour of the bright palladium electrode toward the redox systems $Cr_2O_7^{2-}/Fe^{2+}$ and Ce^{4+}/Fe^{2+} (in potentiometric titration) has been investigated as a function of pretreatment of the electrode. Anodization of the electrode at potentials higher than 800 mV increases ΔE at the equivalence point by 300–400 mV for the dichromate titration. The sharp change in potential is due to the reaction between PdO_2 and Fe^{2+}. The equivalence point corresponds to the beginning of the potential drop, rather than the inflexion point, especially for dilute solutions. If the electrode is ignited before use the surface oxide PdO is oxidized to PdO_2 by Cr(V), the potential increases during the titration and ΔE is 200 mV bigger than when an untreated electrode is used. In the titration of Ce^{4+} with Fe^{2+} the ΔE is largest with untreated electrodes, and if the anodized electrode is used, the titration curves clearly show the reaction between PdO_2 and Fe^{2+}.

NOBLE METAL electrodes (Pt, Pd, Au, Ir, Rh, Ru, Os), by subjection to various treatments (chemical and electrochemical oxidations and reductions, heating in a flame, *etc*), can be brought into different states, which influence the electrode processes on the metal surface. The bright palladium electrode is much used in various electrochemical procedures. Several techniques have been used to obtain information about the state of the surface of pretreated palladium electrodes, including charging curves[1–6]; potential sweep curves;[7] steady-state galvanostatic oxygen overvoltage curves in acid[8,9] and alkaline[9–12] solutions; steady-state potentiostatic polarization,[8] and rest-potential measurements.[13–16]

The surface composition of the anodized palladium electrode has been investigated in some detail. The anodic pretreatment may result in the formation of PdO and PdO_2 on the electrode surface, depending on the anodization potential used. The rest-potential has been established for the systems PdO_2/Pd (1·47 V) and PdO/Pd (0·87 V) in sulphuric acid; these values are characteristic for the systems named. The simultaneous presence of both palladium oxides (PdO_2 and PdO) on the surface results in the occurrence of a mixed potential, the value of which depends on the relative amounts of the two oxides on the surface, and lies between 1·10 and 1·40 V.[13]

We are interested in the response time of differently pretreated palladium electrodes, when they are dipped into dichromate, ceric sulphate and ferrous sulphate solutions,[17–18] and the possibility of their use as indicating electrodes in automatic potentiometric titration.

EXPERIMENTAL

A palladium wire (length 1 cm, diameter 0·5 mm) and a palladium plate (0·5 cm^2 surface area) sealed in a glass tube, were used as electrodes. The $FeSO_4$, $K_2Cr_2O_7$ and $Ce(SO_4)_2$ solutions were prepared from analytical grade reagents with doubly distilled water.

The electrodes were subjected to potentiostatic (anodic and cathodic) pretreatment, by using the Radelkis-R OH-102 polarograph as a source of constant potential. Other pretreatments used were the chemical reduction and flame ignition of the electrode (in the oxidizing part of a methane flame).

All the measurements were made at a temperature of 22 ± 1°. The saturated calomel electrode (SCE) was used as reference electrode, but the potential values were recalculated and are given with respect to the normal hydrogen electrode (NHE) in the same solution. The behaviour of the electrode was characterized by the potential as a function of time, the pretreated electrode being dipped into 0·1 and 0·001*N* solutions of the three reagents, and the potential recorded with the same polarograph. For comparison, similar curves were recorded for an untreated palladium electrode.

The treated electrodes were used as indicating electrodes in redox titrations. Direct or derivative potentiometric curves were recorded, by using an automatic burette with a flow-rate of 3 ml/min. The titration curves were characterized by dE/dV or the volume V_i of titrant added, at the inflexion point.

RESULTS AND DISCUSSION

Response times in $K_2Cr_2O_7$ *solution*

Untreated electrodes. The initial potential of the palladium electrode in contact with a dichromate solution depends on the state of its surface. The untreated electrode, introduced into 0·1*N* dichromate, shows after a few seconds a constant Nernstian potential for the $Cr_2O_7^{2-}/Cr^{3+}$ couple (1080–1090 mV). For somewhat more dilute solutions the potential is 1090 mV, but for 0·001*N* solution it is only 920 mV.

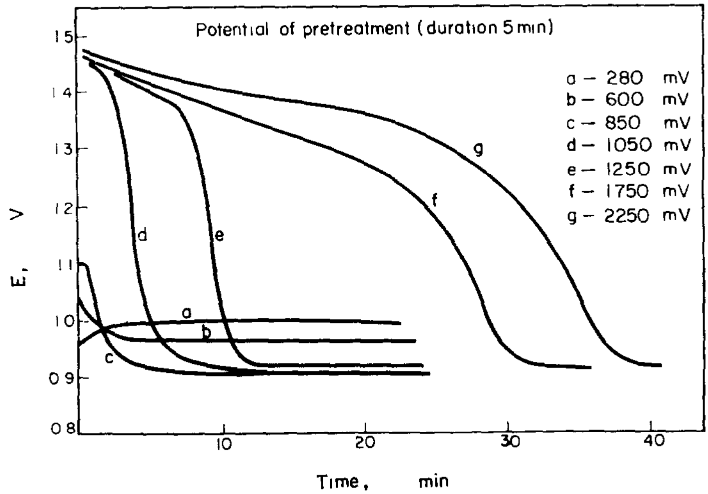


FIG. 1.—The potential–time variation of a preanodized electrode introduced into 0·1*N* $K_2Cr_2O_7$.

Chemically reduced electrode. After chemical reduction (by standing in ferrous sulphate solution) a palladium electrode shows a potential–time behaviour, in 0·1*N* dichromate, similar to that of an untreated electrode, the rest-potential showing a slight increase during the first 10–20 sec (presumably owing to oxidation of ferrous ions adsorbed on the palladium surface) and then remains constant at 1090 mV.

Preanodized electrode. The electrode was preanodized in either 1*N* sulphuric acid or 0·1*N* dichromate in 1*N* sulphuric acid. The $E = f(t)$ curves for electrodes anodized for 5 min at potentials between 0·2 and 2·25 V are shown in Fig. 1. It can be seen that if the pretreatment potential was under 0·80 V, the electrode behaves almost as an untreated electrode. Only at higher potentials are palladium oxides formed on the electrode surface[6] and these are responsible for the potential variations described by curves *d*–*g*.

The potential-time behaviour of an electrode preanodized at 2·25 V in 0·1N dichromate for various time intervals is shown in Fig. 2. The curves show that the longer the pretreatment the longer the rest-potential of the electrode remains high; this can be explained by the dependence between the amount of surface oxide formed and the duration of pretreatment.

When severe pretreatment conditions are used (2·25 V for 60 min) the rest potential remains at 1470–1500 mV for a longer time (Fig. 2, curve *f*) and then decreases rather abruptly, as expected[6] for a PdO_2/Pd system. It can be assumed that under these conditions the electrode behaviour is determined practically only by the PdO_2/Pd system. Intermediate pretreatment conditions (0·80–1·75 V) result in smoothly decreasing rest-potentials (Fig. 1, curves *c* and *d*) which can be interpreted in terms of mixed potentials due to the simultaneous presence of both PdO_2 and PdO (present in variable proportions) on the electrode surface.

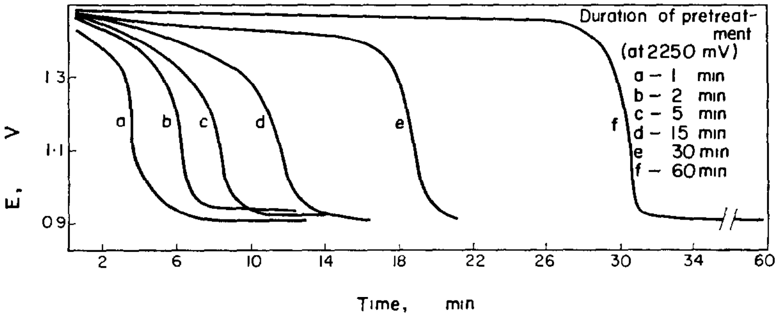


FIG. 2.—The potential–time variation of a preanodized electrode introduced into 0·1N $K_2Cr_2O_7$.

Thermally treated electrode. The electrode was heated for 1–5 min in the oxidizing part of a methane flame having a temperature of *ca.* 900°. The electrode potential is 1150–1200 mV, which suggests that some palladium oxides are present on the surface, but decreases (Fig. 3) to about 900 mV, presumably because of gradual decomposition of PdO_2 in the acidic medium.

Electrochemically reduced electrode. The potential of an electrode placed in dichromate solution after reduction by cathodic treatment in 1N sulphuric acid, depends upon the duration of the pretreatment and the current density used. If the cathodic pretreatment is stopped after the surface oxide has been reduced, the electrode obtained behaves like an untreated one. If the treatment is continued, however, a palladium–hydrogen electrode[18] is obtained, owing to the sorption of hydrogen by the metal. The rest-potential of such an electrode is negative with respect to the SCE, but increases as the hydrogen is lost from the metal by diffusion.

Response times in $Ce(SO_4)_2$ *solution*

Regardless of the type of pretreatment (no treatment at all, potentiostatic polarization at potentials between 0·20 and 2·00 V, ignition, or chemical reduction) the potential of the electrode in 0·1N ceric sulphate is 1470–1500 mV, is not influenced by stirring, and reaches this value in about 4 min. Thus, the palladium electrode shows essentially the potential of the Ce^{4+}/Ce^{3+} system in 1N sulphuric acid. A similar situation occurs for 0·001N ceric sulphate but the potential is about 1·4 V, owing to the dilution effect.

Response time in $FeSO_4$ *solution*

The behaviour of the pretreated electrode is the most interesting in this case, since the surface palladium oxides formed during the anodic pretreatment are reduced by the ferrous sulphate. The reduction rate of the surface oxide layer by iron(II) can readily be followed by recording the potential–time curves. Results for 0·1*N* and 0·01*N* ferrous sulphate are shown in Figs. 4 and 5. The potential decreases from 1470 mV (characteristic for the PdO_2/Pd system) to 700 mV (characteristic for the Fe^{3+}/Fe^{2+} system), at a rate dependent on the intensity of pretreatment and on the concentration of ferrous sulphate. For 0·1*M* iron(II) the potential of the Fe^{3+}/Fe^{2+} system is achieved in 10 sec, but in more dilute solutions (0·001*M*) it takes *ca.* 90 sec.

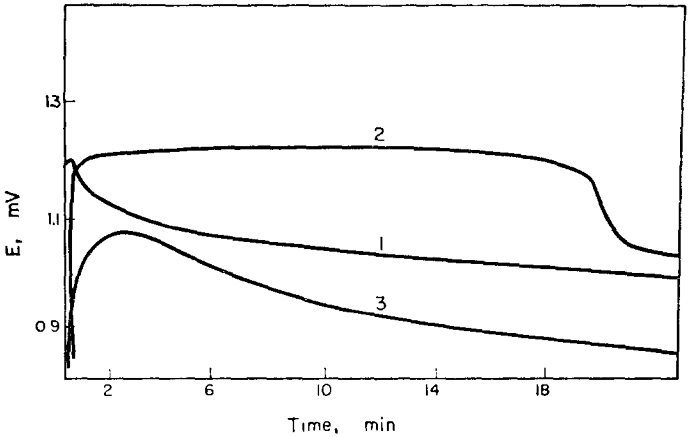


FIG. 3.—The potential–time variation of an ignited electrode introduced into $K_2Cr_2O_7$
1. Ignited for 30 sec; 0·1*N* $K_2Cr_2O_7$.
2. Ignited for 5 min; 0·1*N* $K_2Cr_2O_7$.
3. Ignited for 1 min; 0·001*N* $K_2Cr_2O_7$.

In effect the $E = f(t)$ curves can be considered as describing a "titration" of the surface palladium oxide with ferrous sulphate. No quantitative determinations were made, but these curves could, in principle, be used to determine the amount of surface palladium oxide formed during the pretreatment.

Palladium as an indicator electrode

The results presented above were used in some titration experiments in which the palladium electrode served as an indicating electrode. Since the surface palladium dioxide is unstable,[2,6] automatic potentiometric titrations were made, which are rather rapid (*ca.* 90 sec) and thus permit investigation of the influence of the state of the metal surface on its behaviour as an indicating electrode.

Titration of dichromate with iron(II). The curves for 0·1*N* dichromate titrated with 0·1*M* iron(II) are shown in Fig. 6. With an untreated electrode (curve 2) the potential change follows almost the normal course, with a break of about 400 mV. The cathodically treated electrode (curve 1) also gives a "classical" curve with a much smaller potential break.

If the electrode is preanodized at potentials higher than 800 mV, the electrode potential before the equivalence point is determined by the PdO_2/Pd and/or PdO/Pd systems and is 1·40–1·50 V, much higher than the 1·10 V of the untreated electrode.

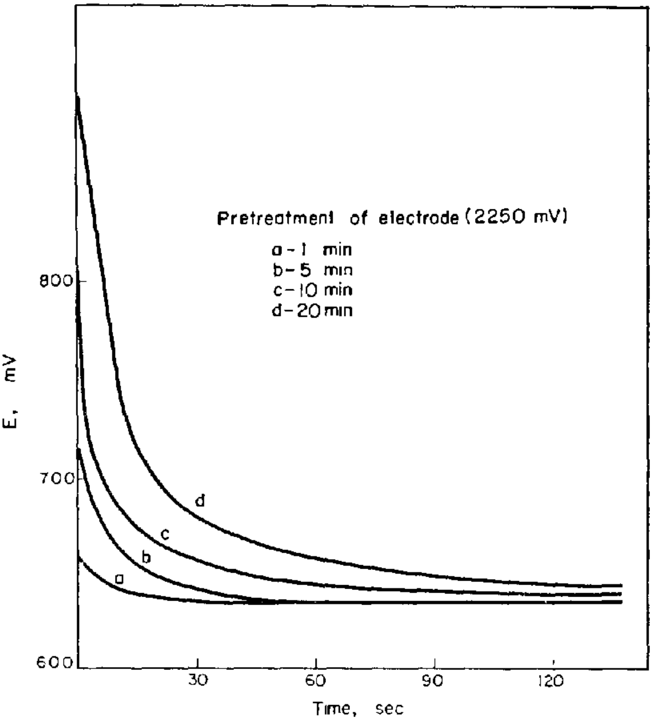


FIG. 4.—The potential-time variation of a preanodized electrode introduced into $0{\cdot}1N$ $FeSO_4$.

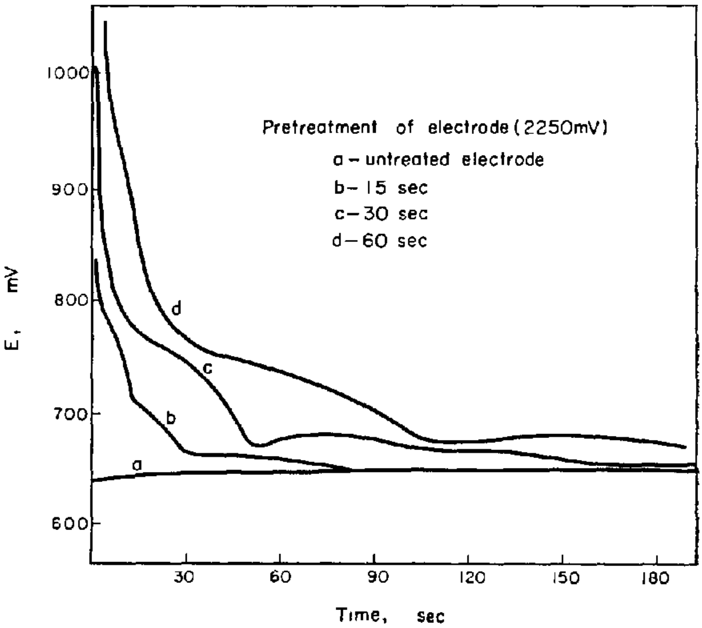


FIG. 5.—The potential-time variation of a preanodized electrode in $0{\cdot}01M$ $FeSO_4$.

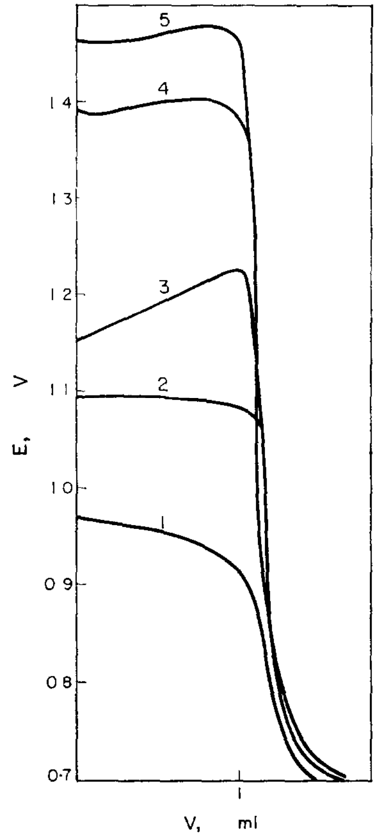


FIG. 6.—Potentiometric titration of 0·1N $Cr_2O_7^{2-}$ with 0·1M Fe^{2+}.

1. Pd cathodically reduced for 10 min at 10 μA.
2. Pd untreated.
3. Pd ignited for 30 sec at ~900°C.
4. Pd anodized for 1 min at 2·25 V.
5. Pd anodized for 5 min at 2·25 V.

The ferrous sulphate reduces the dichromate, but the electrode potential does not follow the change of composition of the titrated solution. Only *after* the equivalence point will the ferrous ions, now in excess, react with PdO_2 (which is still present on the electrode surface, as demonstrated by the high value of the potential at the equivalence point (curves 4 and 5) according to

$$PdO_2 + 4Fe^{2+} + 4H^+ = Pd + 4Fe^{3+} + 2H_2O$$

and the electrode show the potential of the Fe^{3+}/Fe^{2+} system. The potential after the equivalence point decreases from about 1·45 V to about 0·75 V, giving a ΔE of about 700 mV, almost twice that with the untreated electrode. It follows from this mechanism that the equivalence point should be taken as the point at which a sudden decrease of potential occurs, rather than the inflexion point of the titration curve. This is more evident for dilute solutions, as discussed below.

The thermally ignited electrode shows more unusual behaviour (curve 3), the potential first increasing by about 200 mV. This increase is more pronounced with

0·1*N* dichromate and is lower for more dilute dichromate solutions. Since the effect is not observed in the titration of ceric sulphate, the $Cr_2O_7^{2-}/Cr^{3+}$ system must be responsible for this initial increase, presumably because of an increase in the PdO_2/PdO ratio on the electrode surface. Probably PdO_2 is formed by oxidation of the surface PdO (formed during the thermal ignition) by some chemical species, more oxidizing than $Cr_2O_7^{2-}$, which is formed during the reduction of Cr(VI). In a kinetic study of the reduction of dichromate with iron(II), Espenson and King[19] suggested a multi-step mechanism, in which the oxidation states Cr(V) and Cr(IV) occur, the rate-determining step being the Cr(V) → Cr(IV) stage. Since Cr(V) is a stronger oxidizing species than Cr(VI), it seems reasonable to assume that Cr(V) oxidizes the surface PdO to PdO_2, thus causing the initial increase of the electrode potential. After the equivalence point, owing to the reduction of PdO_2 by iron(II), the potential decreases abruptly, as for the anodized electrode. The value of ΔE at the equivalence point is 200–250 mV larger for the ignited electrode than for the untreated electrode.

When 0·01*N* solutions were titrated, similar titration curves were obtained but because ΔE near the equivalence point is determined by the reaction between PdO_2 and iron(II), the end-point indicated by the inflexion point (maximum dE/dV) is shifted from the equivalence point if a preanodized or ignited electrode is used. This effect becomes more pronounced with increasing dilution of the solutions (Tables I and II).

Titration of ceric sulphate with iron(II). The titration curves for this system are classical in shape, irrespective of electrode pretreatment, except that the cathodically reduced electrode gives a variation in the shape of the curve before the equivalence point. The starting potential in titrations with this electrode depends on the time

TABLE I.—TITRATION OF 0·01*N* DICHROMATE WITH 0·01*M* IRON(II)

Electrode treatment	$E°$, *mV*	$(dE/dV)_{\text{inflexion}}$	V*, *ml*
None	1018	120	2·61
None	1090	135	2·61
12 hr in $FeSO_4$	850	20	2.60
Ignited	1160	180	2·61
Anodized 1 min at 2·25 V	1420	180	2·66
Anodized 10 min at 2·25 V	1436	two peaks	2·65
			2·87
Anodized 60 min at 2·25 V	1420	two peaks	2·87
			3·02

* Volume of titrant added at inflexion point.

TABLE II.—TITRATION OF 0·001*N* DICHROMATE WITH 0·001*M* IRON(II)

Electrode treatment	$E°$, *mV*	$(dE/dV)_{\text{inflexion}}$	V*, *ml*
None	922	20	3·37
12 hr in $FeSO_4$	826	15	3·25
Ignited	906	20	3·37
Anodized 10 min at 1·25 V	1450	two peaks	3·41
		65	4·21
Anodized 10 min at 1·75 V	1450	two peaks	3·41
		80	4·20

* Volume of titrant added at inflexion point.

interval between stopping the cathodic pretreatment and beginning the titration. If the electrode is used immediately after pretreatment, the inflexion point appears earlier than with the untreated electrode. The preanodized electrode gives an inflexion point later than that with the untreated electrode, and the break is not as steep. A similar effect was observed in the titration of dichromate with an intensively anodized electrode (30 min at 2·25 V in 0·1*N* dichromate).

Titration of 0·001*N* solutions, with an electrode preanodized in 1*N* sulphuric acid, gives two end-points on the derivative curve, indicating two superimposed electrode processes (Fig. 7). The first corresponds to the titration of cerium(IV) with iron(II) and the second to reduction of surface PdO_2 after the equivalence point.

CONCLUSIONS

Dichromate titration

The preanodization of a bright palladium electrode at potentials higher than 800 mV dramatically increases the potential change around the equivalence point (300–400 mV more than with an untreated electrode) in the titration of 0·1*N* dichromate with ferrous sulphate solution. This dramatic increase of $(\Delta E)v_i$ is due to the reaction between iron(II) and palladium oxides deposited by preanodization of the indicating electrode. These oxides function at the titration as *auxilliary redox systems*. The equivalence point corresponds to the beginning of the potential drop, especially with more dilute solutions (0·001*N*).

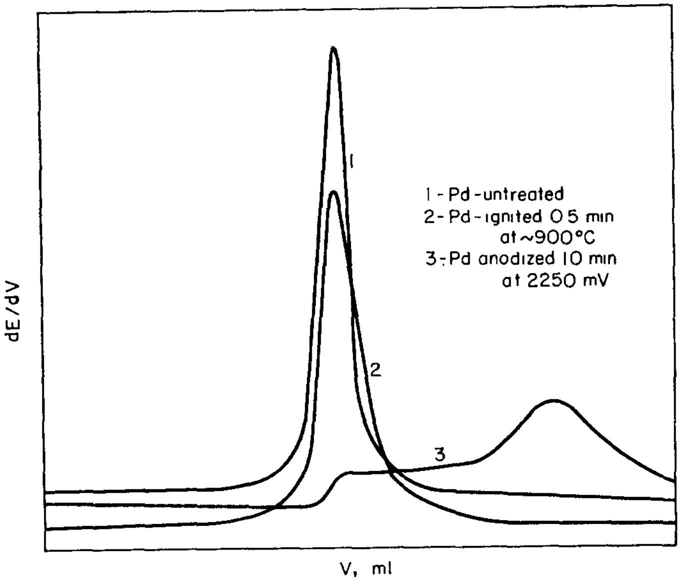


FIG. 7.—Derivative potentiometric titration of 0·001*M* Ce^{4+} with 0·001*M* Fe^{2+}.

The use of a chemically reduced palladium electrode offers no advantage over the untreated electrode. A cathodically reduced electrode behaves like a palladium-hydrogen electrode and gives negative errors.

A thermally treated electrode behaves almost like a preanodized electrode, owing to the oxidation of the surface oxide PdO to PdO_2 by Cr(V) during the titration.

Cerium(IV) *titration*

The untreated electrode gives the largest potential change at the equivalence point. Preanodization results in a less steep curve at the inflexion point, and two processes are involved, one of which is the reduction of PdO_2 by iron(II) after the end-point.

Zusammenfassung—Das Verhalten der blanken Palladiumelektrode gegenüber den Redoxsystemen $Cr_2O_7^{2-}/Fe^{2+}$ und Ce^{4+}/Fe^{2+} (bei potentiometrischer Titration) wurde in Abhängigkeit von der Vorbehandlung der Elektrode untersucht. Anodische Belastung der Elektrode bei Potentialen über 800 mV erhöht den ΔE-Wert am Äquivalenzpunkt der Dichromat-Titration um 300–400 mV. Die scharfe Potentialänderung beruht auf der Reaktion von PdO_2 und Fe^{2+}. Der Äquivalenzpunkt entspricht eher dem Beginn des Potentialabfalls als dem Wendepunkt, besonders bei verdünnten Lösungen. Wird die Elektrode vor dem Gebrauch erwärmt, so wird das Oberflächenoxid PdO durch Cr(V) zu PdO_2 oxidiert, das Potential steigt während der Titration und ΔE ist 200 mV größer als bei Verwendung einer unbehandelten Elektrode. Bei der Titration von Ce^{4+} mit Fe^{2+} ist ΔE bei unbehandelten Elektroden am größten; bei Verwendung der anodisch belasteten Elektrode zeigen die Titrationskurven deutlich die Reaktion zwischen PdO_2 und Fe^{2+}.

Résumé—On a étudié le comportement de l'électrode de palladium poli vis-à-vis des systèmes redox $Cr_2O_7^{2-}/Fe^{2+}$ et Ce^{4+}/Fe^{2+} (en titrage potentiométrique) en fonction du prétraitement de l'électrode. L'anodisation de l'électrode à des potentiels supérieurs à 800 mV accroît ΔE au point d'équivalence de 300–400 mV pour le titrage du bichromate. Le changement net en potentiel est dû à la réaction entre PdO_2 et Fe^{2+}. Le point d'équivalence correspond au début de la chute de potentiel, plutôt qu'au point d'inflexion, particulièrement pour les solutions diluées. Si l'électrode est chauffée avant usage, l'oxyde de surface PdO est oxydé en PdO_2 par Cr(V), le potentiel croît durant le titrage et ΔE est de 200 mV plus grand que lorsqu'on utilise une électrode non traitée. Dans le titrage de Ce^{4+} avec Fe^{2+}, la valeur de ΔE est la plus grande avec des électrodes non traitées, et si l'on utilise l'électrode anodisée, les courbes de titrage montrent clairement la réaction entre PdO_2 et Fe^{2+}.

REFERENCES

1. T. R. Blackburn and J. J. Lingane, *J. Electroanal. Chem.*, 1963, **5**, 216.
2. J. A. V. Butter and G. Drover, *Trans. Faraday Soc.*, 1936, **32**, 427.
3. S. E. S. El Wakkad and A. M. S. Din, *J. Chem. Soc.*, 1954, 3094.
4. A. Hickling and G. G. Vrjosak, *Trans. Faraday Soc.*, 1961, **57**, 123.
5. Yu. A. Mazitov, K. I. Rosental and V. I. Veselovskii, *Dokl. Akad. Nauk SSSR*, 1963, **148**, 152; *Zh. Fiz. Khim.*, 1964, **38**, 151.
6. K. J. Vetter and D. Berndt, *Z. Elektrochem.*, 1958, **62**, 378.
7. F. G. Will and C. A. Knorr, *ibid.*, 1960, **64**, 270.
8. J. P. Hoare, *J. Electrochem. Soc.*, 1965, **112**, 1129.
9. J. J. MacDonald and B. E. Conway, *Proc. Roy. Soc.*, 1962, **A269**, 419.
10. A. Hickling and S. Hill, *Discussions Faraday Soc.*, 1945, **1**, 263; *Trans. Faraday Soc.*, 1950, **46**, 550.
11. Yu. M. Povarov, A. M. Trukhan and P. D. Lukovstov, *Elektrokhimiya*, 1970, **6**, 602.
12. A. G. Poliak, Iu. B. Vasiliev and V. S. Bagotski, *ibid.*, 1970, **6**, 602.
13. J. P. Hoare, *J. Electrochem. Soc.*, 1964, **111**, 610.
14. S. Uneri and M. Kabasakaloglu, *Commun. Fac. Sci. Univ. Ankara, Ser. B*, 1969, **16**, 1.
15. T. N. Andersen and H. Eyring, *J. Phys. Chem.*, 1963, **67**, 92.
16. S. Schuldiner and R. M. Roe, *J. Electrochem. Soc.*, 1964, **111**, 369.
17. C. Liteanu and I. Haiduc, *Stud. Univ. Babeş-Bolyai. Ser. Chim.*, 1971, **16**, 121.
18. *Idem, Rev. Roumaine Chim.*, 1970, **15**, 1555.
19. J. H. Espenson and E. L. King, *J. Am. Chem. Soc.*, 1963, **85**, 3325.

Talanta, 1972, Vol. 19, pp. 1019 to 1023. Pergamon Press. Printed in Northern Ireland

QUANTITATIVE SEPARATION OF Al, Ga, In, AND Tl BY CATION EXCHANGE CHROMATOGRAPHY IN HYDROCHLORIC ACID–ACETONE*

F. W. E. STRELOW and A. H. VICTOR
National Chemical Research Laboratory, P.O. Box 395, Pretoria, South Africa

(*Received* 30 *September* 1971. *Accepted* 12 *November* 1971)

Summary—Up to 4 mmole (1 mmole each) of tervalent Al, Ga, In and Tl are separated from each other on a 60-ml column of AG50W-X8 resin of 200–400 mesh particle size by cation-exchange chromatography in hydrochloric acid–acetone mixtures. Separations are very sharp and without tailing. Recoveries for amounts from 1–100 mg average 100·0 ± 0·1% for the analysis of synthetic mixtures. An anion-exchange method is described for the separation of gallium from the hydrochloric acid–acetone eluate. Relevant cation-exchange distribution coefficients, anion-exchange coefficients for gallium in hydrochloric acid–acetone, an elution curve for all four elements and results of quantitative separations of synthetic mixtures are presented.

THE ONLY ION-EXCHANGE method described in the literature which provides a complete separation of the group IIIA elements Al, Ga, In and Tl in a single column run seems to be that of Kraus *et al.*[1] which uses an anion-exchange resin in the chloride form and involves the elution of the elements with aqueous hydrochloric acid according to the stability of their chloride complexes. The method has the weakness that in 7*M* hydrochloric acid, the eluting agent used for aluminium, indium has a distribution coefficient of only about 20. This causes an early appearance of indium in the eluate and makes separation of large amounts of indium impossible unless comparatively large columns are used. In addition, indium shows appreciable tailing and thallium very strong tailing. Quantitative aspects of the separation have unfortunately not been investigated, but it seems probable that the tailing could lead to incomplete recoveries of thallium and indium unless very large elution volumes are used.

Some information is available on the separation of pairs of the elements mentioned above. Kocheva[2] has separated gallium and indium by eluting the gallium from Dowex 1-X8 resin with 0·5*M* potassium iodide while indium is retained, and Kocheva *et al.*[3] have separated gallium from aluminium by cation-exchange and by anion-exchange using potassium thiocyanate–hydrochloric acid mixtures. Klement *et al.*[4] have eluted indium from a Dowex 50 cation-exchanger with 0·4*M* hydrochloric acid while gallium is retained and Tsintsevich *et al.*[5] have used 3% oxalic acid solution at pH 4 to elute gallium from a Russian cation-exchange resin, aluminium being retained.

In hydrochloric acid containing an organic solvent, differences in chloride complex formation and hence in separation factors are often considerably enhanced. Fritz *et al.*[6] have determined cation-exchange distribution coefficients for 14 elements in hydrochloric acid–acetone and have shown that indium can be separated from aluminium by elution with 0·5*M* hydrochloric acid in 40% aqueous acetone with a separation factor considerably larger than in aqueous hydrochloric acid. Coefficients for gallium and

---

* This is part of a D.Sc. thesis by the second author at the department of Inorganic and Analytical Chemistry of the University of Pretoria.

indium in hydrochloric acid–organic solvent mixtures have been determined by Alimarin *et al.*[7] and Gorokhova *et al.*,[8,9] using Russian resins, and various conditions for separation ranging from 0·1*M* hydrochloric acid in 80% aqueous acetone to 0·75*M* hydrochloric acid in 20% acetone have been presented. Korkisch *et al.*[10] have separated indium, gallium and aluminium by anion-exchange chromatography in hydrochloric acid–acetone and hydrochloric acid-2-methoxyethanol mixtures. Since the distribution coefficients are not very high under the experimental conditions employed, long columns (75 cm) have to be used. Furthermore, results of recovery tests do not seem to be very accurate.

A recent systematic study of cation-exchange distribution coefficients[11] suggested that a separation of all four elements in a single run and with considerably larger distribution coefficients than those obtained by Kraus[1] or Korkisch[10] might be possible by using cation-exchange chromatography in hydrochloric acid–acetone. Favourable distribution coefficients do not always guarantee a good separation, because they cannot predict features of column behaviour such as tailing. The quantitative aspects of the separation of the group IIIA elements was therefore investigated in detail by preparing elution curves and carrying out column experiments with synthetic mixtures.

EXPERIMENTAL

Reagents

Chemicals of analytical-reagent grade purity were used throughout. The resins used were the AG50W-X8 cation-exchanger and AG1-X8 anion-exchanger (BioRad Laboratories, Richmond, California). Resin of 100–200 mesh was used for determination of distribution coefficients and of 200–400 mesh for column work. Borosilicate glass tubes of 20 mm bore with fused-in glass sinters of No. 2 porosity, a burette tap at the bottom and a B19 ground-glass joint at the top, were used as columns.

Distribution coefficients

The relevant cation-exchange distribution coefficients have been published previously,[11] but are included in Table I together with relevant intermediate coefficients obtained from plots of known coefficients[11] against acetone concentration.

TABLE I.—CATION-EXCHANGE DISTRIBUTION COEFFICIENTS IN HCl–ACETONE

Element	0·1*M* HCl + 50% acetone	0·5*M* HCl + 50% acetone	0·5*M* HCl + 90% acetone	2·0*M* HCl + 70% acetone
Tl(III)	0·5	0·5	<0·5	<0·5
In	240	2·0	<0·5	<0·5
Ga	$>10^4$	780	1·9	<0·5
Al	$>10^4$	910	1250	75

Because it was found that gallium is slightly volatile when solutions containing gallium, acetone and hydrochloric acid are evaporated on the water-bath, the possibility of separating gallium from acetone by anion-exchange was investigated. Table II shows relevant distribution coefficients for 1 mmole of gallium in 250 ml of hydrochloric acid containing various amounts of acetone after equilibration with 2·500 g of dry AGI-X8 resin.

TABLE II.—ANION-EXCHANGE DISTRIBUTION COEFFICIENTS FOR Ga IN HCl–ACETONE

	Acetone							
HCl, *M*	0%	20%	40%	60%	70%	75%	80%	90%
0·5	1·0	1·9	9·0	18·9	6·1	3·3	2·2	1·1
1·0	2·2	10·0	52·7	22·3	3·5	2·2	1·1	—
2·0	6·2	47	286	20·0	5·0	3·6	—	—

Elution curve

The conditions suggested by the distribution coefficients in Table I were selected for the quantitative separation. Hydrochloric acid (0·5*M*) in 90% acetone gives a larger separation factor for the Ga–Al pair than 2·0*M* hydrochloric acid in 70% acetone, but the latter eluent shows practically no tailing of gallium and was preferred for this reason. A mixture containing about 0·5 mmole of each element in 25 ml of 0·1*M* hydrochloric acid containing 50% acetone and a small amount of chlorine to keep thallium in the tervalent state was placed on a column of 60 ml of AG50W-X8 resin of 200–400 mesh particle size. The resin column was 19 cm in length, 2·0 cm in diameter and had been equilibrated with 0·1*M* hydrochloric acid in 50% acetone. The cations were washed onto the column with 0·1*M* hydrochloric acid in 50% acetone containing a small amount of chlorine, and thallium(III) was eluted with 200 ml of the same reagent. Indium was then eluted with 300 ml of 0·5*M* hydrochloric acid in 50% acetone, followed by gallium with 300 ml of 2·0*M* hydrochloric acid in 70% acetone, and finally aluminium with 300 ml of 3·0*M* aqueous hydrochloric acid. The flow-rates were about 2·0 ± 0·3 ml for Tl(III) and In and about 3·0 ± 0·3 ml for Ga and Al. Fractions of 25-ml volume were taken with an automatic fractionater and analysed. The experimental curve is shown in Fig. 1.

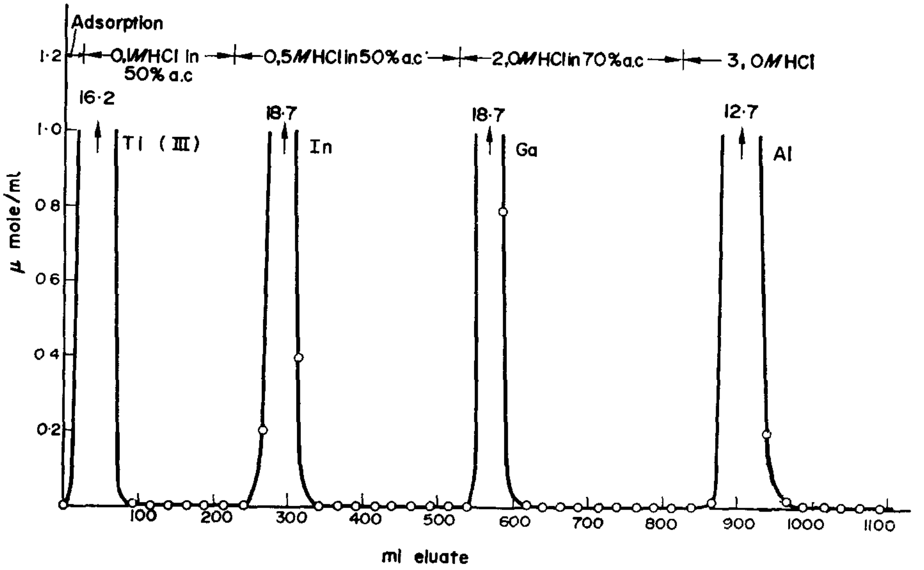


FIG. 1.—Elution of Al, Ga, In and Tl(III).

Quantitative separations

Volumes of standard solutions of two adjacent elements or of all four elements in 0·1*M* hydrochloric acid were measured out in triplicate and hydrochloric acid and acetone were added to give the desired concentrations. The solutions were adsorbed on a column containing 60 ml of AG50W-X8 resin of 200–400 mesh particle size in the hydrogen form which had previously been equilibrated with 0·1*M* hydrochloric acid in 50% acetone. The elements were then eluted with the same sequence of reagents as described above. The eluates were kept separately and the elements determined after the excess of solvent had been removed by evaporation. A special procedure had to be adopted in the case of gallium, because it was found that between 1 and 2% of the gallium present was lost by volatilization. No gallium was lost in control experiments in which aqueous hydrochloric acid solutions were evaporated on the water-bath. The gallium-containing eluate was therefore collected in a 500-ml separating funnel containing 180 ml of 2*M* hydrochloric acid. The solution was mixed and passed through a column containing 45 ml of AG1-X8 anion-exchange resin previously equilibrated with 2*M* hydrochloric acid in 40% acetone. From the mixture (2*M* hydrochloric acid in 44% acetone) gallium was adsorbed with a distribution coefficient of about 240 (Table II), and could then be eluted with 300 ml of 0·1*M* hydrochloric acid. Thallium was partly reduced during the evaporation of excess of eluting agent and had to be reoxidized to thallium(III) with chlorine or bromine. Small amounts of organic matter resulting from the polymerization of acetone were destroyed by evaporation with nitric acid plus 2 ml of perchloric acid. The analytical methods are summarized in Table III and the results are presented in Table IV.

TABLE III.—ANALYTICAL PROCEDURES

Element	Method
Tl(III)	Excess of DCTA, back-titration with Zn(II), Xylenol Orange as indicator. Small amounts spectrophotometrically with Alizarin Red S (elution curves).
Ga	Excess of EDTA, back-titration with Zn(II), Xylenol Orange as indicator. Small amounts spectrophotometrically with Xylenol Orange at pH 5·5 and 515 nm (elution curves).
In	Excess of EDTA, back-titration with Zn(II), Xylenol Orange as indicator. Small amounts by atomic-absorption spectrometry (elution curves).
Tl(III)	Titration with EDTA in the presence of tartrate at pH 10, Methylthymol Blue as indicator.

TABLE IV.—RESULTS OF QUANTITATIVE SEPARATIONS OF SYNTHETIC MIXTURES

Taken				Found*			
Element	*mg*	Element	*mg*	Element	*mg*	Element	*mg*
Tl	20·24	In	232·2	Tl	20·24 ± 0·03	In	232·2 ± 0·2
Tl	404·8	In	11·61	Tl	404·8 ± 0·4	In	11·61 ± 0·02
In	11·61	Ga	142·9	In	11·61 ± 0·02	Ga	142·8 ± 0·2
In	232·2	Ga	7·15	In	232 ± 0·2	Ga	7·15 ± 0·02
Ga	7·15	Al	56·56	Ga	7·15 ± 0·02	Al	56·57 ± 0·05
Ga	142·9	Al	5·66	Ga	142·9 ± 0·2	Al	5·66 ± 0·01
Tl	202·4			Tl	202·3 ± 0·2		
In	116·1			In	116·2 ± 0·1		
Ga	71·46			Ga	71·45 ± 0·05		
Al	28·28			Al	28·29 ± 0·02		

* Mean of triplicate determinations with calculated standard deviations.

DISCUSSION

The method described provides a useful means for the quantitative separation of the group IIIA elements (from Al to Tl) in a single column run. The presence of acetone makes the separation factors considerably higher than those for aqueous hydrochloric acid media. That for the Al–Ga pair is enhanced to more than 150 in $2M$ hydrochloric acid containing 70% acetone as compared with about 1·6 in aqueous $2M$ hydrochloric acid. In $0{\cdot}5M$ hydrochloric acid containing 90% acetone the separation factor for the same pair is larger than 600, but more tailing occurs.

Separations are very sharp and quantitative and tailing is practically non-existent with a 200–400 mesh resin. This is demonstrated on the elution curve shown in Fig. 1, which has been enlarged in the vertical direction to show the sharpness of the tail ends. The method thus compares favourably with the anion-exchange procedures of Kraus *et al.*[1] and Korkisch *et al.*,[10] which show considerably more tailing. Recoveries in the analysis of synthetic mixtures (Table IV) are excellent and average 100·0 ± 0·1% for amounts from 1 to 100 mg. The accuracy of the analysis results for synthetic mixtures is mainly dependent on the accuracy of the method of determination because this introduces the major part of the error.

The additional anion adsorption step for the separation of gallium from solutions containing large amounts of acetone is necessary for accurate work, otherwise gallium recoveries will only be about 98–99%. When the method is applied to semiconductor alloys containing group IIIA elements as well as arsenic, the arsenic will accompany the thallium, and can be separated by an additional anion-exchange step when required. Even at room temperature As(III) is extremely volatile from hydrochloric acid containing more acetone and is partially lost even from drops falling from the tip of the column into a beaker. For complete recovery the tip should dip into a fair volume of water containing sulphide.

When large amounts of thallium are present, Tl(III) tends to be reduced and may precipitate as TlCl in the column, apparently because the chlorine or bromine added initially is slowly used up by reaction with the acetone. In such cases it is better to elute thallium with aqueous 0·1*M* hydrobromic acid containing a little free bromine. In, Ga and Al are also strongly retained under these conditions and the bromide complexes of Tl(III) are considerably more stable to reduction than the chloride complexes.

Zusammenfassung—Bis zu 4 mMol (je 1 mMol) dreiwertiges Al, Ga, In und Tl werden an einer 60 ml-Säule AG50W-X8-Harz der Teilchengröße 200–400 mesh durch Kationenaustauschchromatographie in Salzsäure-Aceton-Gemischen voneinander getrennt. Die Trennungen sind sehr scharf und verlaufen ohne Schwanzbildung. In Testmischungen werden durchschnittlich 100,0 ± 0,1 % bei Mengen von 1–100 mg wiedergefunden. Ein Anionenaustauschverfahren zur Abtrennung von Gallium aus dem Salzsäure-Aceton-Eluat wird beschrieben. Die wesentlichen Kationenaustausch Verteilungskoeffizienten, die Anionenaustauschkoeffizienten für Gallium in Aceton-Salzsäure und eine Elutionskurve für alle vier Elemente und die Ergebnisse quantitativer Trennungen von Testmischungen werden angegeben.

Résumé—On sépare l'un de l'autre jusqu'à 4 mmoles (1 mmole de chaque) d'Al, Ga, In et Tl trivalents sur une colonne de 60 ml de résine AG50W-X8 de dimensions de particule 200–400 mailles par chromatographie d'échange de cations en milieux acide chlorhydrique-acétone Les séparations sont très nettes et sans traînées. Les récupérations pour des quantités de 1–100 mg s'établissent en moyenne à 100,0 ± 0,1 % pour l'analyse de mélanges synthétiques. On décrit une méthode d'échange d'anions pour la séparation du gallium de l'éluat acide chlorhydrique-acétone. On présente les coefficients de partage échange de cations et les coefficients d'échange d'anions concernant le gallium en acide chlorhydrique-acétone, une courbe d'élution pour les quatre éléments, et les résultats de séparations quantitatives de mélanges synthétiques.

REFERENCES

1. K. A. Kraus, F. Nelson and G. W. Smith, *J. Phys. Chem.*, 1954, **58,** 11.
2. L. L. Kocheva, *Compt. Rend. Acad. Bulgare. Sci.*, 1969, **22,** 447; *Chem. Abstr.*, 1969, **71,** 260.
3. L. L. Kocheva and R. Draganova, *Godishnik. Sofiiskiya. Univ., Khun. Fak.*, 1967/68, **62,** 129; *Chem. Abstr.* 1971, **74,** 480.
4. R. Klement and H. Sandmann, *Z. Anal. Chem.*, 1955, **145,** 325.
5. E. P. Tsintsevich, I. P. Alimarin and L. F. Marchenkova, *Vestn. Mosk. Univ., Ser. Mat. Mekhan., Astron., Fiz. Khim*, 1958, **13,** 221; *Chem. Abstr.*, 1959, **53,** 10898.
6. J. S. Fritz and T. A. Rettig, *Anal. Chem.*, 1962, **34,** 1562.
7. I. P. Alimarin, E. P. Tsintsevich and A. N. Gorokhova, *Vestn. Mosk. Univ., Ser. II: Khim*, 1964, **19,** 54; *Chem. Abstr.*, 1964, **61,** 11368.
8. A. N. Gorokhova, I. P. Alimarin and E. P. Tsintsevich, *Zh. Neorgan. Khim.*, 1966, **11,** 191, *Chem. Abstr.*, 1966, **64,** 8964.
9. A. N. Gorokhova, I. P. Alimarin and E. P. Tsintsevich, *Vestn. Mosk. Univ., Ser. II.*, 1966, **21,** 73; *Chem. Abstr.*, 1966, **65,** 61322.
10. J. Korkisch and I. Hazan, *Anal. Chem.*, 1964, **36,** 2308.
11. F. W. E. Strelow, A. H. Victor, C. R. van Zyl and C. Eloff, *ibid.*, 1971, **43,** 870.

Talanta, 1972, Vol. 19, pp. 1025 to 1031. Pergamon Press. Printed in Northern Ireland

SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN ALKALINE SOLUTIONS AND EVALUATION OF SOME HYDROXY-SUBSTITUTED 1,10-PHENANTHROLINES AS CHROMOGENIC REAGENTS

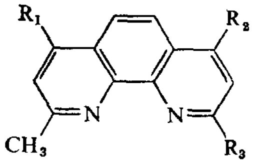
W. E. DUNBAR and A. A. SCHILT
Department of Chemistry, Michael Faraday Laboratories,
Northern Illinois University, DeKalb, Illinois 60115, U.S.A.

(*Received* 6 *December* 1971. *Accepted* 6 *January* 1972)

Summary—Seven new hydroxy-substituted 1,10-phenanthroline derivatives have been evaluated as chromogenic reagents for the determination of copper in strongly alkaline solution. The most sensitive of these, 2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline, has proven to be highly effective in a simple, rapid procedure for determining trace amounts of copper in sodium hydroxide, potassium carbonate, sodium phosphate or ammonium hydroxide.

DISCOVERY of the extraordinary ability of 4,7-dihydroxy-1,10-phenanthroline to form a stable iron(II) chelate in concentrated, even saturated, sodium hydroxide solutions led to its study and use as a chromogenic reagent for the determination of iron in strongly alkaline substances.[1] Moreover, it called attention to the desirability of incorporating hydroxy groups in substituted 1,10-phenanthrolines as a promising means of extending their usefulness as metal chelate ligands to higher pH regions. Contrary to the findings of an earlier study,[2] the presence of a hydroxy group in 1,10-phenanthroline enhances its co-ordination affinity towards iron(II), provided that solutions are strongly alkaline and that an effective reductant, such as sodium hydrosulphite, is employed to prevent atmospheric oxidation of the iron(II).[3]

One of the more promising possibilities, with regard to utilizing the effect of hydroxy substituents, was the modification of the highly selective copper reagents cuproine (2,2′-biquinoline) and neocuproine (2,9-dimethyl-1,10-phenanthroline). By introduction of hydroxy groups into the structures of these important analytical reagents their applicability should be extended to strongly alkaline solutions, thereby eliminating the disadvantages associated with the necessity for neutralization and pH adjustment. However, synthetic problems proved formidable, and progress has been slow. The first success was achieved by Case and Lesser in 1966, who prepared the dihydroxy derivative of cuproine (4,4′-dihydroxy-2,2′-biquinoline).[4] Fulfilling expectations, this compound proved to be a highly effective chelation reagent for copper in concentrated alkaline solutions.[5] More recently, Case succeeded in the difficult synthesis of a number of 4-hydroxy and 4,7-dihydroxy-1,10-phenanthrolines, including the long sought-for neocuproine derivative 2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline.[6] These phenanthrolines, and their characterization as analytical reagents, are the subject of this paper. Each of the seven identified below will be referred to hereafter by a Roman numeral.



Compound	R_1	R_2	R_3	*Name (prefix) of substituted* 1,10-*phenanthroline*
I	OH	OH	CH_3	2,9-dimethyl-4,7-dihydroxy-
II	OH	OH	C_6H_5	2-methyl-4,7-dihydroxy-9-phenyl-
III	OH	OCH_3	CH_3	2,9-dimethyl-4-hydroxy-7-methoxy-
IV	OCH_3	OH	C_6H_5	2-methyl-4-methoxy-7-hydroxy-9-phenyl-
V	OH	H	CH_3	2,9-dimethyl-4-hydroxy-
VI	H	OH	C_6H_5	2-methyl-7-hydroxy-9-phenyl-
VII	OH	CH_3	CH_3	2,7,9-trimethyl-4-hydroxy-

EXPERIMENTAL

Apparatus and reagents

A Cary Model 14 recording spectrophotometer and a Corning Model 7 pH meter with saturated calomel and glass electrodes were used for spectral and pH measurements respectively.

The substituted phenanthrolines were samples of the original analysed samples synthesized and reported by Case.[6] Solutions (0·01*M*) of these were prepared by dissolving weighed amounts in measured volumes of 95% ethanol.

Standard copper sulphate solution containing 0·1589 mg of Cu/g was prepared by dissolving pure copper in nitric acid, fuming with sulphuric acid, cooling and adding water to give a known concentration. The 10% hydroxylamine hydrochloride solution was prepared by dissolving 100 g of the salt in 900 g of water. All chemicals were reagent quality, except for the isopentanol, which was purified grade.

Absorption spectra

Solution conditions and pH for maximum colour development in the copper reaction of each new phenanthroline derivative were determined. These were reproduced in preparing solutions for spectral examination when determining the visible absorption characteristics of the copper complexes.

Solutions of the copper(I) complexes of the dihydroxy derivatives (compounds I and II) were prepared by delivering weighed amounts of the standard copper solution into 10-ml volumetric flasks, followed by 1 ml of 10% hydroxylamine hydrochloride solution, 5 ml of 8*M* sodium hydroxide, 2 ml of 0·01*M* phenanthroline derivative, and sufficient distilled water to dilute to volume. Copper(II) solutions were prepared similarly, but without hydroxylamine hydrochloride.

The copper(I) complexes of the monohydroxy derivatives (compounds III–VII) proved to be insoluble in aqueous solutions, so extraction into isopentanol was employed to prepare solutions for spectral examination. Weighed samples of the copper solution were delivered into 60-ml separatory funnels, followed by addition of 2 ml of 10% hydroxylamine hydrochloride solution, 20 ml of 5*M* sodium hydroxide, and 1 ml of the 0·01*M* phenanthroline derivative (in the order cited). After mixing, the contents were extracted first with a 5-ml and then a 1-ml portion of isopentanol. The extracts were combined in a 10-ml volumetric flask and diluted to volume with 95% ethyl alcohol.

Spectra of the prepared solutions and of appropriate blanks were recorded *vs.* air, using a 1·00-cm silica cell. Wavelengths of maximum absorbance, molar absorptivities, and conformity to Beer's law were determined.

Identity and stability of complexes

The method of continuous variations[7] and the mole-ratio method[8] were employed to determine the ligand to metal ratios of the copper(I) and (II) complexes of compounds I and II. For all four complexes, within experimental error, the results indicated two ligand molecules per copper ion. Lack of curvature in the plotted results precluded reliable calculation of formation constants but indicated very high stability for all four complexes.

Acid dissociation constants of compound I were determined from ultraviolet spectral measurements of solutions of various pH containing identical concentrations of I.

Recommended procedure for determination of copper

Transfer a sample (by weight or volume, and of sufficient size to provide a concentration of 1–6*M* hydroxide ion on final dilution) into a 25-ml volumetric flask. If the sample is a carbonate, phosphate, or only a moderately strong base (or does not have the requisite hydroxide ion content), add 5 ml of 5*M* sodium hydroxide to the flask. Add 2 ml of 10% hydroxylamine hydrochloride solution and 4 ml of $2 \times 10^{-3}M$ 2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline in 0·1*M* sodium hydroxide. Dilute to volume with distilled water, and measure the absorbance in either a 1·00- or 10·0-cm cell (depending on copper content) at 400 nm against a reagent blank.

RESULTS AND DISCUSSION

All seven of the investigated compounds readily form intense yellow or orange complexes with copper(I) in solutions of pH 11 and higher. The copper(I) complexes of the monohydroxy derivatives, compounds **III–VII**, are insoluble in aqueous solution, soluble in aqueous ethanol, and quantitatively extractable into isopentanol. Compounds **I** and **II**, the dihydroxy derivatives, yield water-soluble copper(I) complexes that are not extractable into isopentanol unless an appropriate cation, such as tetrabutylammonium, is present in relatively high concentration.

Less intensely coloured complexes are formed by the seven compounds in reactions with copper(II). The dihydroxy derivatives form blue, water-soluble complexes extractable into isopentanol, from solutions of pH 11 and higher. The monohydroxy compounds yield blue-green soluble copper(II) complexes from solutions of pH 6–9, and much less coloured but stable complexes in more alkaline solutions.

Spectra of the copper(I) and copper(II) complexes of compound **I**, the most sensitive chromogen of the group, are shown in Fig. 1. Wavelengths of maximum absorbance, and molar absorptivities, of the copper complexes of all seven chromogens are listed in Table I. Ranging from 8300 to 11,500 $\mathrm{l.mole^{-1}.cm^{-1}}$, the molar absorptivities are higher than the value of 7,000 found for the complex of 4,4′-dihydroxy-2,2′-biquinoline.[5] This is as expected, since copper(I)–phenanthroline complexes commonly exhibit greater absorptivities than their biquinoline analogues. On the basis of its superior chromogenic properties, as well as other interesting aspects, compound **I** was selected for more extensive investigation and analytical application.

The copper(I) and copper(II) complexes of **I** are both bis-chelates, as shown by the results of mole-ratio and continuous-variations measurements. For both complexes, the most reasonable structure would involve two bidentate ligands with their molecular planes at right angles and their nitrogen atoms co-ordinated in a tetrahedral configuration about copper. The high stability of the complexes, as shown by the completeness of reaction when small but stoichiometric amounts are mixed, even in concentrated sodium hydroxide, argues against other co-ordination modes or structures, all of which, as models show, would involve considerable steric hindrance or strain.

The ionic charge on either of the copper complexes of **I** depends on the extent of ionization of the hydroxy groups, which is governed by pH. In order to predict charge magnitudes, p*K* values for the dissociation of **I** were determined by ultraviolet spectrophotometry. Three sets of isosbestic points are consecutively produced on changing the pH of an aqueous solution of **I** from 0 to 14, demonstrating the existence of three dissociation steps and four acid–base species of **I**. From pH 0 to 5, isosbestic points at 255 and 277 nm are observed, representative of the dissociation of an acid of $pK = 2$, presumably the protonated phenanthroline species $(CH_3)_2(OH)_2phen \cdot H^+$.

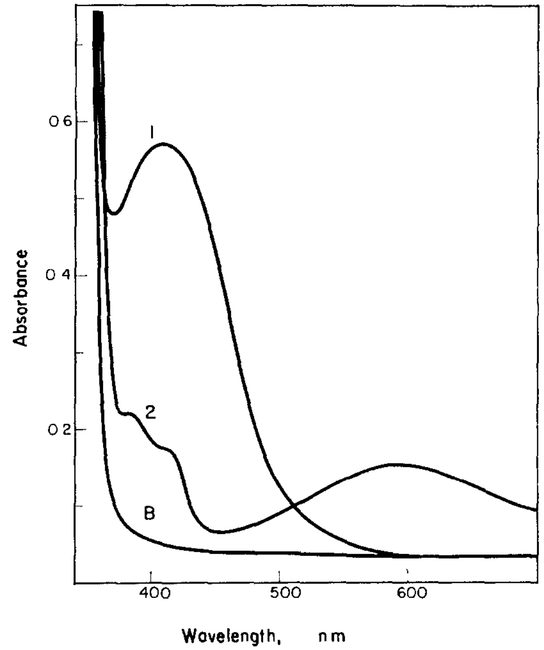


FIG. 1.—Visible absorption spectra of the copper(I) complex (curve 1), copper(II) complex (curve 2) of 2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline and reagent blank (curve B). Both copper complexes are $4{\cdot}34 \times 10^{-5}M$, measured in 1·00 cm cell *vs.* air.

Over the pH range 2–11, with isosbestic points at 244 and 265 nm, the results are indicative of the dissociation of an acid of $pK = 7{\cdot}5$, believed to be the un-ionized phenanthroline or its zwitterion $(CH_3)_2(OH)(O)^{-}phen \cdot H^+$. Above pH 11, an isosbestic point at 245 nm is displayed, presumed to be associated with the final ionization or deprotonation step:

$$(CH_3)_2(OH)(O)phen^- \rightleftharpoons (CH_3)_2(O)_2phen^{2-} + H^+$$

The p*K* value for this step could not be determined precisely, because of the high pH, and alkaline error of the glass electrode. An estimate, based on hydroxide concentration rather than pH, gives a p*K* value of the order of 13. It is, therefore, concluded that **I** exists predominantly as a doubly charged anion, with both hydroxy protons ionized, in solutions of hydroxide ion concentrations of 1*M* or greater. If the bound ligands ionize to the same degree as the free ligand, then the copper(I) complex exists as $[CuI_2]^{3-}$ and the copper(II) as $[CuI_2]^{2-}$.

Since pH determines the degree of ionization of the hydroxy groups of the bound ligands, and thus the ionic charge on the copper complexes of **I**, it should also affect the spectra and extractability of the complexes. The effect on spectra is especially evident over the pH range from 11 to 13. However, in sodium hydroxide solutions of concentration 1*M* or greater only minor changes in spectra occur, which supports the conclusion that ionization of the hydroxy groups is essentially complete above pH 13. The results are given in Table II. For analytical purposes it is fortunate that the

TABLE I.—VISIBLE ABSORPTION CHARACTERISTICS OF COPPER COMPLEXES

Compound	Cu(I) complex			Copper(II) complex		
	Solvent	λ_{max}, nm	ε*	Solvent	λ_{max}, nm	ε*
I	4*M* NaOH	400	11,500	4*M* NaOH	590	3,000
II	4*M* NaOH	400	10,400	4*M* NaOH	610	2,200
III	Isopentanol	420	10,500	pH 8(H_2O)	606	2,030
IV	Isopentanol	412	8,970	pH 8(H_2O)	612	1,850
V	Isopentanol	462	8,400	pH 8(H_2O)	618	1,490
VI	Isopentanol	437	8,300	pH 8(H_2O)	612	1,400
VII	Isopentanol	456	9,000	pH 8(H_2O)	614	1,250

* $l.mole^{-1} cm^{-1}$.

TABLE II.—4,7-DIHYDROXY-2,9-DIMETHYL-1,10-PHENANTHROLINE, SPECTRAL CHARACTERISTICS OF COPPER COMPLEXES AS A FUNCTION OF NaOH CONCENTRATION

[NaOH], *M*	Copper(II)		Copper(I)	
	λ, nm	ε*	λ, nm	ε*
0·01	580	2,380	400	9,500
0·5	582	2,930	400	10,200
1·0	584	2,940	400	11,400
2	586	3,030	400	11,600
3	590	3,090	400	11,600
4	590	3,020	400	11,500
5	592	3,090	400	11,500
6	594	3,100	400	11,500
7	595	3,200	400	11,500
8	precipitate		precipitate	

* $l.mole^{-1}.cm^{-1}$.

absorbance of the copper(I) complex of **I** is independent of hydroxide ion concentration over a broad range (1–7*M* NaOH). Precipitation of the copper(I) and (II) complexes of **I** from sodium hydroxide more concentrated than 8*M* is curious, and probably a salting-out effect, but not a serious problem for analytical purposes. The effect of pH or hydroxide ion concentration on extractabilities is also interesting. The copper(I) complex of **I** is not extractable at any pH, whereas the extractability of the copper(II) complex into isopentanol increases from essentially zero at pH 12 to quantitative extractability at 3*M* or higher concentration of sodium hydroxide. Such behaviour with increasing sodium hydroxide concentration is believed to be a consequence of increased ion association between sodium ions and the anionic copper(II) complex, leading to greater extractability, rather than a result of increasing ionization and ionic charge of the complex.

The recommended procedure was evaluated for effectiveness and reliability for the determination of copper in four different alkaline substances of commercial importance: sodium hydroxide, potassium carbonate, sodium phosphate, and concentrated ammonium hydroxide. Because of lack of a variety of different samples to test, synthetic samples were prepared by adding known amounts of standard copper solution to weighed samples of the pure alkaline substances. The analytical results are compiled in Table III. Beer's law is obeyed, and the molar absorptivity of the

TABLE III.—DETERMINATION OF COPPER IN ALKALINE SUBSTANCES

Taken, *µg*	Found, *µg*			
	in 3 *g* of NaOH	in 4 *g* of K_2CO_3	in 1 *g* of Na_3PO_4	in 5 *g* of NH_3 (30%)
15·8	14·4	15·6	15·7	16·0
31·6	28·0	31·1	31·6	33·0
47·3	47·6	47·4	48·1	48·8
63·2	64·1	59·4	63·7	64·1
79·1	80·7	80·2	79·6	80·0
110	110	112	115	111
126	128	128	129	124
158	158	158	159	152
Average deviation, *µg*	1·2	1·1	1·4	1·7
Relative standard deviation, %	1·0	0·8	1·0	1·9

copper(I) complex is $11{,}500 \pm 100$ l.mole^{-1}.cm^{-1}, the same for all four media, within experimental error. Colour development is rapid, and no change in absorbance occurs during a one hour period of exposure to the atmosphere. In stoppered flasks the colour is stable for several weeks, and indefinitely if protected against oxygen and carbon dioxide absorption.

Several commonly-encountered substances were tested as possible interferents in the determination of copper. Samples of a 4*M* solution of sodium hydroxide containing 1·90 ppm copper were treated with various amounts of substances added before analysis. None of the following ions, at a concentration of 100 ppm, gave rise to a relative error greater than 1%, and hence these ions do not interfere: acetate, borate, carbonate, halides, halates, oxalate, perchlorate, phosphate, silicate, tartrate, alkali metals, alkaline earth metals, aluminium, ammonium, antimony, arsenic, chromium(III), lead, manganese(II), nickel, and tin(II). Cyanide or sulphide ions cause serious interference, and only 0·01 and 0·1 ppm are tolerated, respectively. If present in excess of 10 ppm, cobalt and zinc interfere by reacting with the chromogenic reagent **I**, larger concentrations are tolerated if more reagent is employed. Iron interferes above 10 ppm and is not masked by addition of tartrate. Its interference can be avoided by modifying the recommended procedure to include an extraction step. If hydroxylamine hydrochloride is omitted, the copper(II) complex can be separated from the iron by extraction with isopentanol followed by back-extraction with 2*M* sodium hydroxide containing hydroxylamine to yield the copper(I) complex for subsequent measurement.

The major advantage of the use of **I** for the determination of copper is that it can be applied directly to alkaline samples without the necessity of neutralization and pH adjustment. This advantage is shared by the closely related copper chromogen 4,4-dihydroxy-2,2′-biquinoline. On comparison, compound **I** (2,9-dimethyl-4,7-dihydroxy-1,10-phenanthroline) is superior in sensitivity and simpler to employ. Unlike its cuproine analogue, the copper(I) complex of **I** is soluble in alkaline solutions, an extraction step or addition of alcohol is unnecessary, and its use in automated procedures is practicable. One disadvantage, common to both chromogens, is that their synthesis is involved and expensive. Fortunately, a small amount suffices for many determinations, so cost should not be a serious deterrent to use.

Zusammenfassung—7 neue Hydroxylderivate von 1,10-Phenanthrolin wurden als Farbreagentien für Kupfer in stark alkalischer Lösung getestet. Das empfindlichste davon, 2,9-Dimethyl-4,7-dihydroxy-1,10-phenanthrolin ist sehr nützlich bei einem einfachen Verfahren zur raschen Bestimmung von Kupferspuren in Natriumhydroxid, Kaliumcarbonat, Natriumphosphat oder Ammoniumhydroxid.

Résumé—On a évalué sept nouveaux dérivés hydroxy substitués de la 1,10-phenanthroline en tant qu'agents chromogènes pour le dosage du cuivre en solution fortement alcaline. Le plus sensible d'entre eux, la 2,9-diméthyl 4,7-dihydroxy 1,10-phénanthroline s'est montrée hautement efficace dans une technique simple et rapide de dosage de traces de cuivre dans la soude, le carbonate de potassium, le phosphate de sodium ou l'ammoniaque.

REFERENCES

1. A. A. Schilt, G. F. Smith and A. Heimbuch, *Anal. Chem.*, 1956, **28**, 809.
2. M. N. Hale and M. G. Mellon, *J. Am. Chem. Soc.*, 1950, **72**, 3217.
3. A. A. Schilt, *Ph.D. Thesis*, University of Illinois, 1956.
4. F. H. Case and J. M. Lesser, *J. Heterocyclic Chem.*, 1966, **3**, 170.
5. A. A. Schilt and W. C. Hoyle, *Anal. Chem.*, 1969, **41**, 344.
6. F. H. Case, *J. Heterocyclic Chem.*, 1970, **7**, 647.
7. W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, 1941, **63**, 437.
8. A. S. Meyers Jr. and G. H. Ayres, *ibid.*, 1957, **79**, 49.

Talanta, 1972, Vol. 19, pp. 1033 to 1042. Pergamon Press. Printed in Northern Ireland

SYNTHESIS AND ION-EXCHANGE PROPERTIES OF THERMALLY STABLE STANNIC SELENITE

MOHSIN QURESHI and SYED ASHFAQ NABI
Z.H. College of Engineering and Technology and Department of Chemistry,
Aligarh Muslim University, Aligarh (U.P.), India

(*Received* 12 *August* 1971. *Accepted* 9 *December* 1971)

Summary—Stannic selenites have been synthesized under a variety of conditions. The most stable sample is prepared by mixing 0·05*M* solutions of stannic chloride and sodium selenite in the ratio of 1:1 at pH 1. It is a bifunctional amorphous material. A tentative structure has been proposed on the basis of chemical composition, pH titrations, infrared and thermogravimetric analyses. Its ion-exchange capacity is 0·75 and 0·73 meq/g after drying at 50° and 500° respectively. Its analytical importance has been established by the following quantitative separations: Cu^{2+} from Ni^{2+}, Co^{2+}, Fe^{3+}, Ga^{3+} and In^{3+}, Fe^{3+} from Pb^{2+} and Sc^{3+}, and Sc^{3+} from VO^{2+}.

THERE ARE two problems yet to be solved despite the large amount of work already carried out on synthetic inorganic ion-exchangers. They are to develop thermally stable ion-exchange materials and to prepare materials which are specific for certain cations. We have synthesized a number of inorganic substances and studied their properties with these ends in view. Cation separations have been achieved on paper impregnated with stannic selenite,[1] but no further studies were made. The present paper describes the synthesis, ion-exchange properties and analytical applications of stannic selenite.

EXPERIMENTAL

The instrumental studies were performed as described in our earlier paper.[2]

Synthesis

Stannic selenite was precipitated by mixing sodium selenite and stannic chloride solutions under the conditions given in Table I. The pH was adjusted by adding either hydrochloric acid or sodium hydroxide solution. On standing for 24 hr the precipitate settled. It was filtered off, washed first with water at the precipitation pH, then with demineralized water at pH 6, and dried in an oven at 50°. The material was converted into the H^+ form. To study the effect of drying temperatures on the ion-exchanger, different portions of one precipitate (Table I, sample 6) were dried at various temperatures.

Chemical stability

The chemical stability was determined as described earlier.[2] The solubilities are given in Tables I and III. Tin and selenium were determined by the phenylfluorone[5] and the diaminobenzidine[6] methods respectively.

Chemical composition

A 200-mg portion of the ion-exchanger was dissolved in 30 ml of hot concentrated hydrochloric acid. The solution was then cooled to room temperature and selenium was precipitated as red selenium metal[3] with sulphur dioxide solution. The precipitate was filtered off and dried at 105° to constant weight. Tin[4] was estimated by titration with potassium dichromate after prior reduction with lead metal.

Ion-exchange capacity

After elution of hydrogen ions with 0·1, 0·5, 1, 2, 3 and 4*M* potassium chloride it was found that optimum results are obtained with 1*M* potassium chloride. The ion-exchange capacity was determined with 1*M* salt solutions as eluents and the results are given in Table II. Topp and Pepper's method[7] was followed for pH titrations (Fig. 1).

TABLE I.—SYNTHESIS AND CHEMICAL STABILITY OF STANNIC SELENITE

Sample	Conditions of synthesis				Appearance in H+ form	Chemical composition Sn/Se	Solubility, *mg*/50 *ml*			
	[$SnCl_4 \cdot 5H_2O$], *M*	[Na_2SeO_3], *M*	Mixing ratio, *v*/*v*	pH			Water		4*M* HNO_3	
							Sn	Se	Sn	Se
1	0·1	0·1	1:1	1	White Semi-transparent	1·44	0·00	0·05	1·2	5·1
2	0·1	0·1	1:2	1	White opaque	1·00	0·06	4·3	3·1	20·5
3	0·1	0·1	2:1	1	White semi-transparent	2·2	0·00	0·08	1·8	5·5
4	0·1	0·1	1:1	3	White	2·1	0·00	0·06	3·0	5·8
5	0·05	0·025	1:1	1	White	1·4	0·00	0·08	1·2	5·8
6	0·05	0·05	1:1	1	White	1·36	0·00	0·03	1·1	5·00

TABLE II.—ION-EXCHANGE CAPACITY (pH 5–6) OF STANNIC SELENITE AT 25°C

Sample	Ion-exchange capacity, *meq*/*g*						
	Li^+	Na^+	K^+	Rb^+	Cs^+	Ba^{2+}	Mg^{2+}
1	0·90	0·75	0·63	0·60	0·60	0·61	0·55
2	1·05	1·16	0·90	1·1	1·20	1·15	0·90
3	0·87	0·65	0·63	0·60	0·55	0·69	0·56
4	0·82	0·61	0·60	0·61	0·75	0·62	0·50
5	0·98	0·67	0·68	0·80	0·71	0·71	0·65
6	1·15	0·96	0·75	0·80	0·71	1·00	0·66

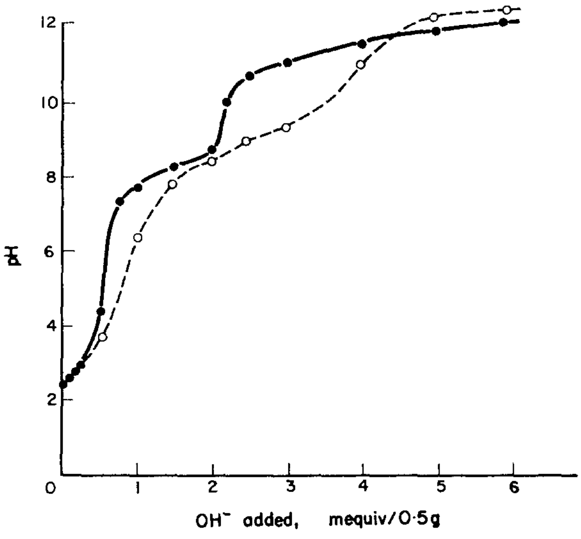


FIG. 1.—pH-titration curve of stannic selenite. (—•—) sample 1, (—○—) sample 6.

Thermal treatment

Thermogravimetric analysis of various samples in the H^+ form was performed at a heating rate of 4°/min. Sample 6 was also analysed in the potassium form (Fig. 2). To examine the effect of drying temperature on the ion-exchange properties of the material, the orginal precipitates of sample 6 were also dried at various temperatures in a muffle furnace for 2 hr.

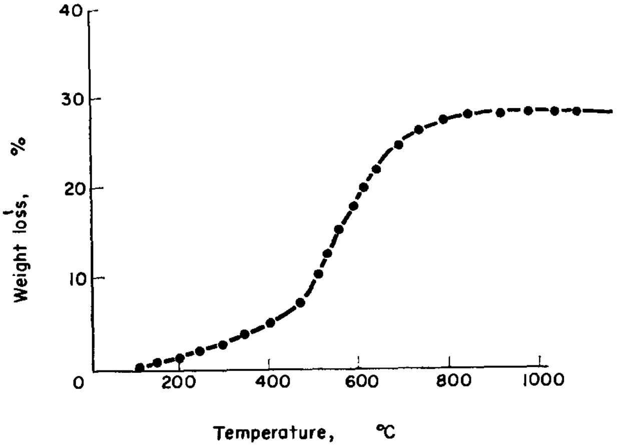


FIG. 2.—Thermogram of stannic selenite (sample 6) in H^+ form.

TABLE III.—EFFECT OF DRYING TEMPERATURE ON SAMPLE 6

Drying temperature, °C	Appearance of beads	Solubility, *mg/50 ml*			
		Water		4*M* HNO_3	
		Sn	Se	Sn	Se
50	White semi-transparent	0·00	0·06	1·8	5·5
100	White	0·00	0·05	1·75	5·8
200	White	0·00	0·06	1·8	5·6
300	Light yellow	0·00	0·06	1·8	5·6
400	Yellow	0·04	0·8	2·5	5·9
500	Yellowish orange	0·4	0·8	2·8	5·9
600	Orange	0·1	1·8	2·8	6·1
700	Light brown	1·3	3·3	5·5	7·5

RESULTS

X-Ray diffraction analysis

X-Ray photographs of samples dried at 50°, nickel-filtered Cu-Kα radiation being used, show that they are amorphous.

Infrared spectra

Infrared spectra were measured by the standard KBr disc technique (Fig. 3).

Distribution coefficient

K_d values for 27 metal ions were determined on samples 1 and 6 in water (pH 6) and $10^{-2}M$ nitric acid as described earlier.[8] In order to explore the effect of drying on the behaviour of the ion-exchanger, distribution coefficients were also determined on

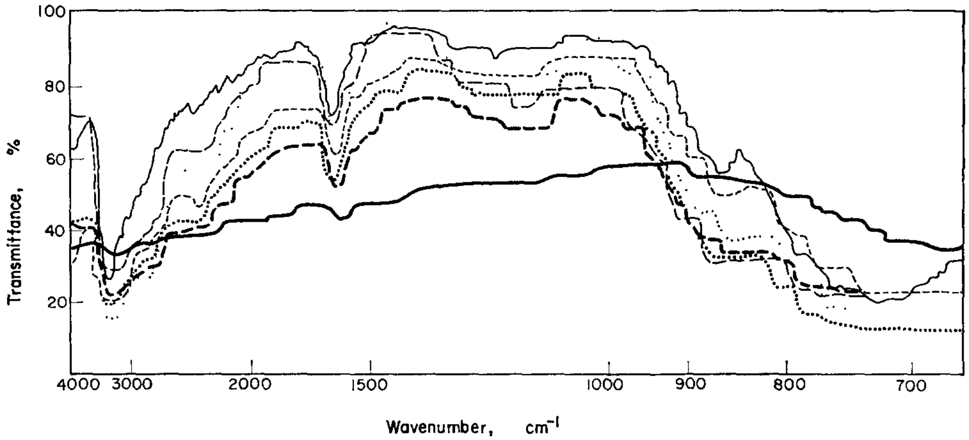


Fig. 3.—Infrared spectra of stannic selenite dried at different temperatures (KBr disc method).

(———) 50°C, (·······) 100°C, (— — —) 200°C, (– – –) 300°C, (· · ·) 400°C, (- - -) 500°C, (━━) 700°C.

materials dried at various temperatures. These results are summarized in Tables IV and V. The sorption of Ba^{2+} and Cu^{2+} was also tested at different pH values.

Quantitative separations of metal ions on stannic selenite columns:

Separations were achieved on columns of 0·6 cm diameter, using 1·5 g of ion-exchanger (100–150 mesh) in the hydrogen form. The flow-rate was 8–10 drops/min. The metal ions in 10-ml fractions of the effluent were estimated by titration with 0·002*M* EDTA. Quantitative separations of Cu(350 μg)–Ni(230 μg), Cu(350 μg)–Co(185 μg), Cu(350 μg)–In(250 μg), Cu(350 μg)–Ga(180 μg), Fe(175 μg)–Sc(162 μg), Fe(175 μg)–Pb(215 μg), Fe(175 μg–Cu(350 μg) and Sc(162 μg)–V(153·6 μg) were achieved and their elution curves are shown in Figs. 4 and 5.

DISCUSSION

Stannic selenite shows an unusual selectivity towards alkali metals. The ion-exchange capacity of sample 1 decreases from 0·9 to 0·6 meq/g on going from Li^+ to Cs^+. On the basis of the radii of the hydrated ions one would expect the reverse order. This reversal is probably due to the specific size of the cavities. A similar case was observed by Torracca and co-workers[9] who found that in zirconium arsenate the cavities play a more dominant role in the exchange process than any other factor. The exchange capacity of stannic selenite samples for K^+ ions varies from 0·6 to 0·77 meq/g at pH 6. The capacity is dependent on the selenite content as the replaceable hydrogen ions are attached to this group. Thus sample 2 has the maximum capacity. This behaviour is similar to that of other inorganic ion-exchangers of this class. Stannic selenite is unique in one respect: on drying the ion-exchanger at elevated temperatures from 50° to 500° there is an almost negligible loss in ion-exchange capacity (Fig. 6). Zirconium tungstate[10] and titanium tungstate[11] on the other hand are much more sensitive in this temperature range and their ion-exchange capacity is almost completely lost on heating them at 100° and 270° respectively. Stannic

TABLE IV.—DISTRIBUTION COEFFICIENTS OF METAL IONS ON STANNIC SELENITE IN WATER (pH 5–6) AND IN $10^{-2}M$ HNO_3

Metal ion	K_d $\frac{mg/g \text{ of resin}}{mg/ml \text{ of solution}}$			
	Sample 1		Sample 6	
	pH 5–6	$10^{-2}M$ HNO_3	pH 5–6	$10^{-2}M$ HNO_3
Cu^{2+}	C.A.	$0{\cdot}95 \times 10^3$	$0{\cdot}23 \times 10^3$	$0{\cdot}85 \times 10^3$
Ni^{2+}	$1{\cdot}90 \times 10^3$	$0{\cdot}54 \times 10^3$	$0{\cdot}42 \times 10^3$	$0{\cdot}17 \times 10^3$
Hg^{2+}	$2{\cdot}26 \times 10^3$	$0{\cdot}56 \times 10^3$	$1{\cdot}88 \times 10^3$	$0{\cdot}30 \times 10^3$
Co^{2+}	$0{\cdot}61 \times 10^3$	$0{\cdot}16 \times 10^3$	$0{\cdot}80 \times 10^3$	$0{\cdot}14 \times 10^3$
Sc^{3+}	$0{\cdot}16 \times 10^3$	$0{\cdot}08 \times 10^3$	$0{\cdot}58 \times 10^3$	$0{\cdot}18 \times 10^3$
Ga^{3+}	$0{\cdot}27 \times 10^3$	$0{\cdot}09 \times 10^3$	$0{\cdot}66 \times 10^3$	$0{\cdot}29 \times 10^3$
Al^{3+}	$0{\cdot}22 \times 10^3$	$0{\cdot}44 \times 10^3$	$1{\cdot}94 \times 10^3$	$0{\cdot}20 \times 10^3$
Fe^{3+}	$0{\cdot}11 \times 10^3$	$0{\cdot}06 \times 10^3$	$0{\cdot}16 \times 10^3$	$0{\cdot}05 \times 10^3$
In^{3+}	$0{\cdot}28 \times 10^3$	$0{\cdot}12 \times 10^3$	$0{\cdot}54 \times 10^3$	$0{\cdot}18 \times 10^3$
Pb^{2+}	$0{\cdot}64 \times 10^3$	$0{\cdot}22 \times 10^3$	$9{\cdot}20 \times 10^3$	$1{\cdot}76 \times 10^3$
Zn^{2+}	$1{\cdot}07 \times 10^3$	$0{\cdot}51 \times 10^3$	$2{\cdot}24 \times 10^3$	$0{\cdot}21 \times 10^3$
Cd^{2+}	$3{\cdot}87 \times 10^3$	$0{\cdot}68 \times 10^3$	$1{\cdot}10 \times 10^3$	$0{\cdot}42 \times 10^3$
Mg^{2+}	$0{\cdot}30 \times 10^3$	$0{\cdot}11 \times 10^3$	$0{\cdot}23 \times 10^3$	$0{\cdot}15 \times 10^3$
Ba^{2+}	C.A.	$0{\cdot}60 \times 10^3$	$3{\cdot}70 \times 10^3$	$0{\cdot}30 \times 10^3$
Sr^{2+}	$4{\cdot}54 \times 10^3$	$0{\cdot}35 \times 10^3$	$1{\cdot}21 \times 10^3$	$0{\cdot}05 \times 10^3$
Ca^{2+}	$3{\cdot}60 \times 10^3$	$0{\cdot}52 \times 10^3$	$0{\cdot}28 \times 10^3$	$0{\cdot}15 \times 10^3$
La^{3+}	C.A.	C.A.	C.A.	C.A.
Y^{3+}	$2{\cdot}47 \times 10^3$	C.A.	$2{\cdot}98 \times 10^3$	$0{\cdot}46 \times 10^3$
Ce^{3+}	C.A.	C.A.	C.A.	$0{\cdot}24 \times 10^3$
Sm^{3+}	C.A.	$3{\cdot}84 \times 10^3$	C.A.	$0{\cdot}23 \times 10^3$
Pr^{3+}	C.A.	$3{\cdot}50 \times 10^3$	C.A.	$0{\cdot}83 \times 10^3$
Nd^{3+}	C.A.	$2{\cdot}25 \times 10^3$	C.A.	$0{\cdot}90 \times 10^3$
VO^{2+}	$0{\cdot}57 \times 10^3$	$0{\cdot}21 \times 10^3$	$2{\cdot}14 \times 10^3$	$0{\cdot}52 \times 10^3$
Th^{4+}	$2{\cdot}40 \times 10^3$	$0{\cdot}96 \times 10^3$	$1{\cdot}65 \times 10^3$	$1{\cdot}20 \times 10^3$
Zr^{4+}	C.A.	C.A.	C.A.	$3{\cdot}88 \times 10^3$
Hf^{4+}	C.A.	$4{\cdot}00 \times 10^3$	C.A.	$3{\cdot}50 \times 10^3$
UO_2^{+}	C.A.	$3{\cdot}02 \times 10^3$	C.A.	$2{\cdot}25 \times 10^3$

C.A. Complete adsorption.

TABLE V.—DISTRIBUTION COEFFICIENTS OF METAL IONS ON STANNIC SELENITE (DRIED AT DIFFERENT TEMPERATURES) IN WATER (pH 5–6)

Metal ion	Drying temperature, °C						
	50	100	200	300	400	500	800
Mg^{2+}	230	525	323	233	293	225	560
Ba^{2+}	$3{\cdot}70 \times 10^3$	$1{\cdot}53 \times 10^3$	$1{\cdot}85 \times 10^3$	$2{\cdot}34 \times 10^3$	$2{\cdot}34 \times 10^3$	$3{\cdot}15 \times 10^3$	$4{\cdot}95 \times 10^3$
Sr^{2+}	$1{\cdot}21 \times 10^3$	$1{\cdot}03 \times 10^3$	750	$2{\cdot}03 \times 10^3$	$0{\cdot}96 \times 10^3$	$1{\cdot}32 \times 10^3$	$1{\cdot}20 \times 10^3$
Ca^{2+}	180	$1{\cdot}17 \times 10^3$	$1{\cdot}26 \times 10^3$	$1{\cdot}50 \times 10^3$	$1{\cdot}80 \times 10^3$	$3{\cdot}70 \times 10^3$	$3{\cdot}88 \times 10^3$
La^{3+}	C.A.	C.A.	C.A.	471	C.A.	C.A.	C.A.
Y^{3+}	$2{\cdot}98 \times 10^3$	C.A.	C.A.	520	$5{\cdot}07 \times 10^3$	C.A.	C.A.
Ce^{3+}	C.A.	C.A.	C.A.	90	C.A.	C.A.	C.A.
Sm^{3+}	C.A.	C.A.	C.A.	537	C.A.	$5{\cdot}95 \times 10^3$	$5{\cdot}97 \times 10^3$
Pr^{3+}	C.A.	C.A.	2700	C.A.	C.A.	C.A.	C.A.
Nd^{3+}	C.A.	C.A.	5100	8	C.A.	C.A.	$4{\cdot}54 \times 10^3$

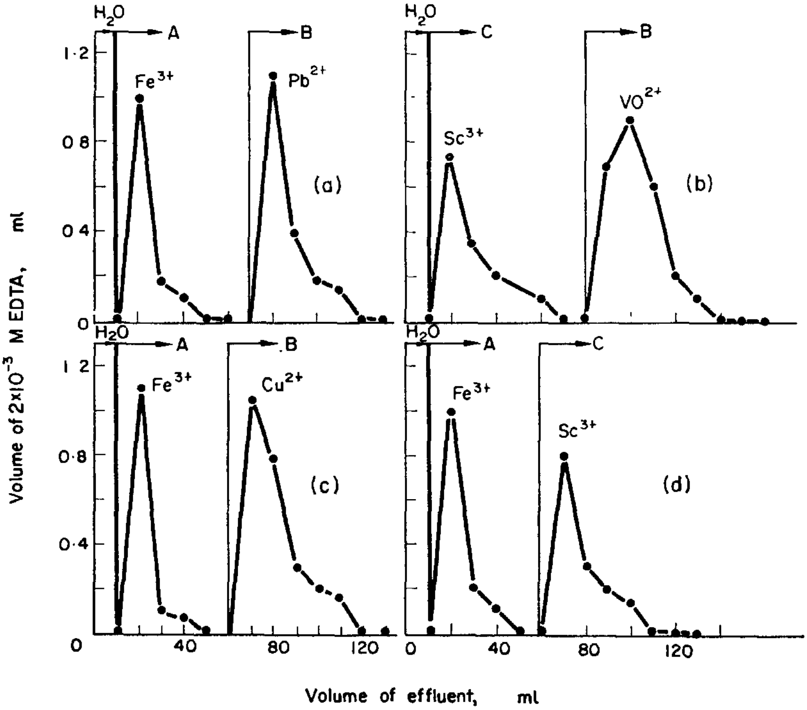


FIG. 4.—Separation of (*a*) Fe^{3+} from Pb^{2+}, (*b*) Sc^{3+} from VO^{2+}, (*c*) Fe^{3+} from Cu^{2+}, (*d*) Fe^{3+} from Sc^{3+}.
A = 0·01*M* HNO_3, B = 6% NH_4NO_3 in 0·1*M* HNO_3, C = 0·1*M* HNO_3.

tungstate[12] and stannic molybdate[13] behave in a similar manner. Stannic selenite is therefore superior to other inorganic ion-exchangers as it can be dried at high temperatures without appreciable loss in ion-exchange capacity.

The following conclusions can be drawn from the K_d values (Tables IV and V). Stannic selenite has a very high affinity for many metal ions, *e.g.*, Zr^{4+}, Hf^{4+}, Th^{4+}, UO_2^+, rare earths, Cu^{2+} and Pb^{2+}, even in acid media. The sequence of adsorption for various ions is found to be $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}:Al^{3+} > Ga^{3+} > In^{3+}:La^{3+} > Ce^{3+} > Y^{3+} > Al^{3+}$ as in the case of zirconium phosphate. The selectivity order for alkaline earth metals follows a pattern $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ similar to that for sulphonic acid resins and also in accordance with the hydrated ion radii, which increase from Ba to Mg.

The effect of drying temperature on distribution coefficients (Table V) reveals many interesting results for alkaline earths and rare earth metals. It can be inferred from the table that the increase in drying temperature from 50° to 300° has very little effect on the K_d values of these metal ions. It is clear that the K_d values generally increase when the drying temperature is raised to 300° and upwards. This characteristic of stannic selenite is in agreement with the measurements of Alberti *et al.*[14] for zirconium phosphate. However, the decrease in K_d values for rare earth metals, especially in the case of Ce^{3+} and Nd^{3+} on exchanger dried at 300°, may be explained by the fact that in addition to condensation, steric and free energy factors sometimes play a significant role which may affect the equilibrium constant. The high uptake on stannic selenite dried at 800° agrees with the findings of Veselý,[15] where obviously no

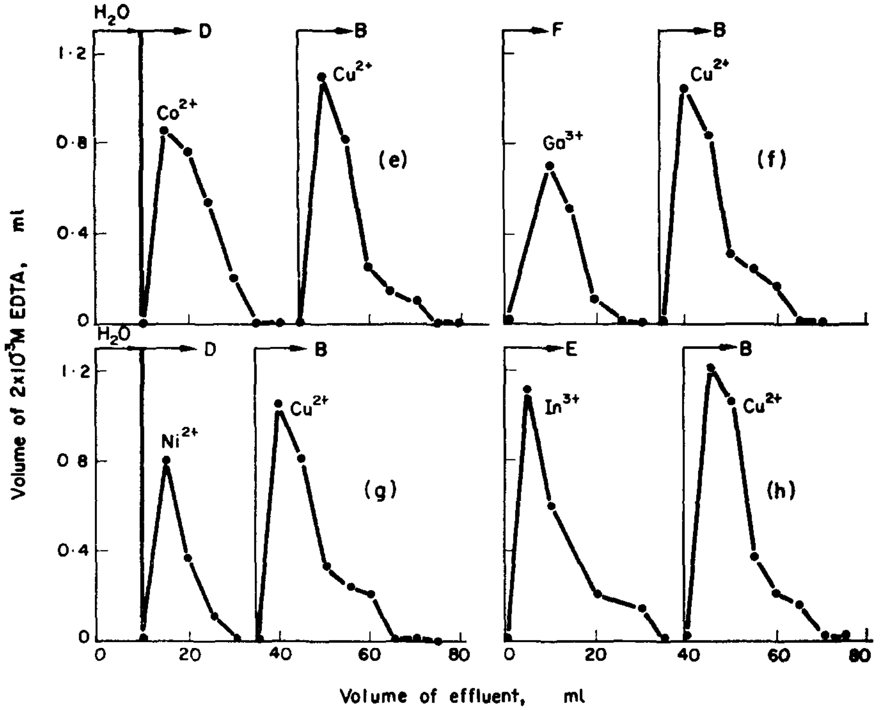


FIG. 5.—Separation of (*e*) Cu^{2+} from Co^{2+}, (*f*) Cu^{2+} from Ga^{3+}, (*g*) Cu^{2+} from Ni^{2+}, (*h*) Cu^{2+} from In^{3+}.

B = 6% NH_4NO_3 in $0{\cdot}1M$ HNO_3, D = $0{\cdot}03M$ HNO_3, E = $0{\cdot}5M$ HNO_3, F = $0{\cdot}05M$ HNO_3.

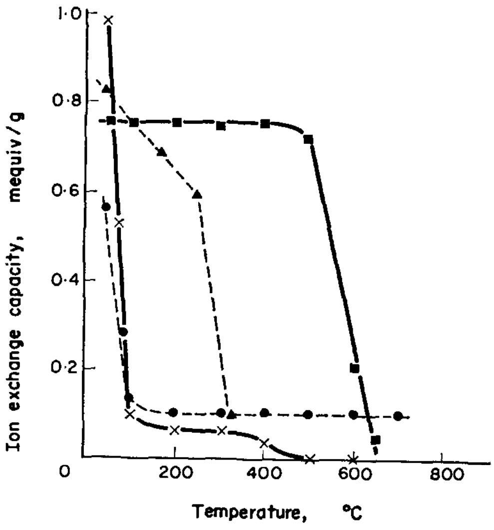


FIG. 6.—Ion-exchange capacity as a function of drying temperature.
(- -●- -●- -) stannic tungstate, (—×—×—) stannic molybdate, (—■—■—) stannic selenite, (- -▲- -▲- -) titanium tungstate.

ion-exchange mechanism is involved and ion-pair formation takes place owing to the conversion of the exchanger into the oxide, as is also evident from the thermogram and ion-exchange capacity data. The absorption sequence for alkaline earth metals on exchanger dried at 500° is $Ca^{2+} > Ba^{2+} > Sr^{2+} > Mg^{2+}$. This behaviour is difficult to explain at this stage as the ion-exchange material is amorphous, but the ions may be retained by a mechanism other than ion-exchange. The variation in K_d values with pH for Ba and Cu ions was also studied. A plot of log K_d *vs.* pH for these ions gave a straight line with a slope of 1 for Ba^{2+} and 1·5 for Cu^{2+}. In an ideal exchange reaction a slope of 2 would be expected for bivalent metal ions. This deviation from the actual value may be due to the simultaneous effect of ion-exchange and other processes, *e.g.*, adsorption. Elution studies showed that most of the hydrogen ions are released from the exchanger with the first 40 ml of the eluent.

Chemical analysis shows that stannic selenite has Sn:Se ratios which vary from 1:1 to 2·2:1. It can be inferred from Table I that the excess of sodium selenite solution in the reaction mixture decreases the tin content in the product (sample 2). Studies have been concentrated on samples 1 and 6 owing to their high ion-exchange capacity and good stability. The composition of sample 6 was found to be Sn:Se = 4:3 and the following formula is tentatively suggested:

$$(SnO)_4(OH)_2(SeO_3)_3 \cdot 6H_2O$$

Thermogravimetric results also provide evidence in support of this formula. The number of water molecules was calculated by the method of Alberti *et al.*[16] The thermogram (Fig. 2) shows two apparent breaks, one at 450° and the other at 775°. There is no change in weight observed on increasing the temperature above 775°. If the formula above is assumed to be correct, the theoretical weight loss due to the removal of 6 water molecules is 10%, in agreement with the experimental value. It may therefore be concluded that the weight loss which continues up to 450° is due to the removal of external water molecules. A sharp increase in weight loss is observed when the temperature is raised to 775°. Significant structural changes must occur over this temperature range and condensation may take place, resulting in the removal of water molecules. Above 775° the weight becomes almost constant owing to the formation of oxides. Infrared absorption spectra and the ion exchange capacity of stannic selenite dried at temperatures above 700° confirm this conclusion.

The infrared absorption spectra of stannic selenite (Fig. 3) dried at various temperatures show three absorption peaks. These spectra, when compared with those of thorium tungstate[2] and stannic arsenate, yield the following interpretation. A very strong peak in the 3800–2900 cm^{-1} region with a maximum at 3400 cm^{-1} represents the interstitial water, free water and OH groups. The strong peak in the region 1700–1500 cm^{-1} is characteristic of interstitial water molecules. The third strong peak in the region 900–700 cm^{-1} may be due to the selenite[17] group. It is interesting to note that infrared spectra of stannic selenite dried at 700° show no absorption peaks and thus confirm the removal of external water molecules and interstitial water from the ion-exchanger.

The pH titration curves give two inflexion points, showing the bifunctional behaviour of the exchanger, which differs from other inorganic ion-exchangers prepared in our laboratory. It can be easily inferred from the curve that the exchanger is not appreciably hydrolysed in acid media. It is also evident that the hydrolysis of sample 1 is more pronounced than that of sample 6 in the pH range 2·5–11, and the reverse holds at above pH 12. Similar types of titration curves are obtained for other samples, except sample 3 which shows only one inflexion point. The molecular weight of 1063 corresponds to a theoretical ion-exchange capacity of 1·8 meq/g and coincides with the practical value at pH 8·2 as obtained from the titration curve.

The exchanger is quite stable in nitric acid and water. Sample 2, in which the Sn:Se ratio is 1:1, seems to be less stable than other samples. It may therefore be inferred that decrease in the tin content decreases the stability. It can also be seen that the drying temperature has little effect on the stability of stannic selenite up to 500°. However, the material appears to be unstable and hydrolyses appreciably if heated above this temperature.

The great affinity and differential selectivity for many metal ions even on drying at high temperatures reveals that stannic selenite is a useful ion-exchanger and a number of separations of metal ions appear possible. Eight binary separations have been achieved quantitatively on a small column (Figs. 4,5).

Acknowledgement—The authors are grateful to Dr. S. M. F. Rahman and Professor Wasiur Rahman for providing research facilities. They also thank Dr. B. Rama Rao and Mr. Irshad Massod for X-ray and TGA work.

Zusammenfassung—Zinn(IV)-selenite wurden unter verschiedenen Bedingungen dargestellt. Das stabilste Präparat erhält man durch Mischen von 0,05*M* Lösungen von Zinn(IV)-chlorid und Natriumselenit im Verhältnis 1:1 bei pH 1. Es ist ein bifunktioneller amorpher Stoff. Auf Grund der chemischen Zusammensetzung, von pH-Titrationen und Infrarot- sowie thermogravimetrischen Analysen wird ein Strukturvorschlag gemacht. Nach Trocknen bei 50° bzw. 500° beträgt die Ionenaustauschkapazität 0,75 bzw. 0,73 mÄq/g. Die analytische Bedeutsamkeit geht aus folgenden quantitativen Trennungen hervor: Cu^{2+} von Ni^{2+}, Co^{2+}, Fe^{3+}, Ga^{3+} und In^{3+}, Fe^{3+} von Pb^{2+} und Sc^{3+} sowie Sc^{3+} von VO^{2+}.

Résumé—On a synthétisé les sélénites stanniques sous diverses conditions. L'échantillon le plus stable est préparé en mélangeant des solutions 0,05*M* de chlorure stannique et de sélénite de sodium dans le rapport 1:1 à pH 1. C'est une substance amorphe bifonctionnelle. On a proposé une structure possible sur la base de la composition chimique, de titrages pH, et d'analyses infrarouge et thermogravimétrique. Sa capacité d'échange d'ions est de 0,75 et 0,73 Meq/g après séchage à 50° et 500° respectivement. On a établi son importance analytique par les séparations quantitatives suivantes: Cu^{2+} de Ni^{2+}, Co^{2+}, Fe^{3+}, Ga^{3+} et In^{3+}, Fe^{3+} de Pb^{2+} et Sc^{3+}, et Sc^{3+} de VO^{2+}.

REFERENCES

1. M. Qureshi, K. N. Mathur and A. H. Israili, *Talanta*, 1969, **16**, 503.
2. M. Qureshi and S. A. Nabi, *J. Chem. Soc.* (*A*), 1971, **1**, 139.
3. C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IC, p. 2980. Elsevier, Amsterdam, 1962.
4. I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. 3, pp. 196, 320. Interscience, New York, 1957.
5. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd. Ed., p. 862. Interscience, New York, 1959.
6. N. H. Furman, *Standard Methods of Chemical Analysis*, 6th Ed., Vol. 1, p. 930. Van Nostrand, Princeton, 1962.
7. N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, 1949, 3299.
8. M. Qureshi and S. A. Nabi, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2059.

9. E. Torracca, U. Costantino and M. A. Massucci, *J. Chromatog.*, 1967, **30**, 584.
10. C. B. Amphlett, *Inorganic Ion Exchangers*, p. 107. Elsevier, New York, 1964.
11. M. Qureshi and J. P. Gupta, *J. Chem. Soc.*, (*A*), 1970, 2620.
12. M. Qureshi and K. G. Varshney, *J. Inorg. Nucl. Chem.*, 1968, **30**, 3081.
13 M. Qureshi and J. P. Rawat, *ibid.*, 1968, **30**, 305.
14. G. Alberti and A. Conte, *Atti Accad. Naz. Lincei, Rend. Classe Sci. Fis., Mat. Nat.*, 1959, **24**, 782, *J. Chromatog.*, 1961, **5**, 244.
15. V. Veselý and V. Pekárek, *J. Inorg. Nucl. Chem.*, 1963, **25**, 697.
16. G. Alberti, P. C. Galli, U. Costantino and E. Torracca, *ibid.*, 1967, **29**, 571.
17. F. A. Miller and C. H. Wilkins, *Anal. Chem.*, 1952, **24**, 1281.

Talanta, 1972, Vol. 19, pp. 1043 to 1048. Pergamon Press. Printed in Northern Ireland

ION-EXCHANGE BEHAVIOUR OF METALS ON DEAE-CELLULOSE IN METHANOL–THIOCYANATE–HYDROCHLORIC ACID MEDIA

ROKURO KURODA, TAKAAKI KONDO and KOICHI OGUMA
Laboratory for Analytical Chemistry, Faculty of Engineering,
University of Chiba, Yayoi-cho, Chiba, Japan

(*Received* 17 *September* 1971. *Accepted* 26 *December* 1971)

Summary—Only a few metals can be adsorbed on DEAE-cellulose from aqueous thiocyanate–chloride media. However, several metal ions, including Cu(II), Zn, Cd, In, Bi and U(VI), exhibit enhanced adsorption on DEAE-cellulose from methanol–thiocyanate–hydrochloric acid mixtures. The distribution coefficients for these metals are given as functions of methanol, ammonium thiocyanate and hydrochloric acid concentration. Differences in adsorption among metals permit many useful separations, including those of two-, three- and four-component mixtures, on short columns containing 1–1·5 g of DEAE-cellulose.

WE HAVE been exploring the possibilities of separating many metals on weakly basic anion-exchangers, particularly DEAE-cellulose(DEAE), both in aqueous media and in mixed aqueous–organic solvent media. Progress in this field has been reviewed in a previous paper[1] and also in a monograph.[2]

Although only a few metals can be adsorbed on DEAE from aqueous solution,[3,4] the addition of a protic solvent such as methanol to nitric[5] and hydrochloric acid[1] solutions improves the adsorption characteristics of nitrato and chloro complexes on DEAE.

We have investigated the adsorption behaviour of a number of metals on DEAE in methanol–thiocyanate–hydrochloric acid media. The number of metals which are adsorbed on DEAE sufficiently to permit their separation on columns is less than the number adsorbed on a strongly basic resin from aqueous thiocyanate–hydrochloric acid media.[6] This provides a basis for developing selective ion-exchange methods.

EXPERIMENTAL

Materials

DEAE(diethylaminoethylcellulose, Serva, 0·74 meq/g) was placed in a large column and treated with 1*M* ammonium thiocyanate adjusted to pH 1 with dilute thiocyanic acid. It was then washed with demineralized water by centrifugation, until the pH of the supernatant liquid was 2·5. After drying at 40° for 2–3 hr, the DEAE was stored in a desiccator over a saturated potassium bromide solution.

Stock solutions of metals were prepared by dissolving appropriate amounts of their salts in 0·5 or 3*M* hydrochloric acid, according to their ease of hydrolysis, to give *ca.* 10 mg of metal/ml.

Equilibrium study

The weight distribution coefficients of Cu(II), Zn, Cd, In, Bi and U(VI) were determined by a batch equilibrium method. The DEAE in the thiocyanate form (0·5 g) was weighed and placed in glass-stoppered conical flasks containing the equivalent of 1 mg each of Zn, Cd, In, Bi or U(VI) and 40 ml of appropriate methanol–ammonium thiocyanate–hydrochloric acid mixtures of various compositions. For Cu(II) 0·30 mg was used to avoid heavy loading. The mixtures were shaken mechanically for 20 hr at 25·0 ± 0·1°. The two phases were separated by filtration and the filtrates were analysed colorimetrically. The distribution coefficient was computed according to the equation:

$$K_d = \frac{\text{(amount of metal in DEAE phase/g of DEAE)}}{\text{(amount of metal in solution phase/ml of solution)}}.$$

Procedure for chromatographic separation

Two types of column (bore 13 mm) containing 1 g and 1·5 g of DEAE are used, the beds being 3 cm and 4·5 cm long, respectively. The columns are pretreated with a methanol–ammonium thiocyanate–hydrochloric acid mixture, the composition of which is the same as that used in the sample preparation. About 5 ml of a sample solution are loaded onto the top of the column, allowed to percolate and then eluted. The individual procedures are shown in Table III and Fig. 3. A flow-rate of 1 ml/min is used throughout.

Analytical methods used for the determination of distribution coefficients and for the effluent analyses are summarised in Table I.

TABLE I.—ANALYTICAL METHODS

Cation	Method
Al	Titration with EDTA, using Cu-PAN* as indicator.
Ni	Colorimetrically with 4-(2-pyridylazo) resorcinol.[7]
Cu(II), Bi	Colorimetrically with diethyldithiocarbamate.[8]
Zn	Colorimetrically with zincon.[9]
Ga	Titration with EDTA, using Cu-PAN as indicator.
Rare earths, U(VI)	Titration with EDTA, using Xylenol Orange as indicator. Traces of the rare earths[10] and U(VI)[11] determined colorimetrically with arsenazo III.
Cd	Titration with EDTA, using Xylenol Orange as indicator. Traces of Cd determined colorimetrically with dithizone.[12]
In	Colorimetrically with Xylenol Orange.[13]

* A mixture of 1-(2-pyridylazo)-2-naphthol and Cu-EDTA.

RESULTS AND DISCUSSION

Adsorption

The distribution coefficients of Cu(II), Zn, In, Bi and U(VI) on DEAE in methanol–ammonium thiocyanate–hydrochloric acid media are indicated in Fig. 1 as a function of methanol concentration, the concentrations of ammonium thiocyanate and hydrochloric acid being kept constant at 1·1*M* and 0·5*M*, respectively. The coefficient increases with increasing concentration of methanol for each metal, indicating the pronounced effect of methanol on the adsorption of thiocyanato complexes on DEAE.

Table II lists the coefficients for Cu(II), Zn, Cd, In, Bi and U(VI) on DEAE as functions of thiocyanate and hydrochloric acid concentrations. Zn, Cd and Bi have already been found to be adsorbed from mixed methanol–hydrochloric acid media.[1] For these metals the coefficient decreases with increasing concentration of thiocyanate, indicating that thiocyanate ions compete with thiocyanato complexes of these metals for the ion-exchange sites. However, the chloride-dependence of the coefficient in the presence of thiocyanate is different with different metals. For example, Zn is adsorbed strongly at lower concentrations of both thiocyanate (0·1*M*) and chloride (0·001–0·01*M*), while Cd is adsorbed weakly under the same conditions.

Pronounced adsorption of Cu(II), In and U(VI) on DEAE was observed when mixed solvent systems involving methanol, thiocyanate and hydrochloric acid were used. In contrast to Zn, Cd and Bi, their coefficients tend to increase with increasing concentration of thiocyanate.

DEAE adsorbs only a limited number of metals from aqueous thiocyanate–chloride media. It is certain that the addition of methanol to the aqueous thiocyanate–chloride media allows Cu(II), Zn, Cd, In, Bi and U(VI) to be adsorbed on DEAE,

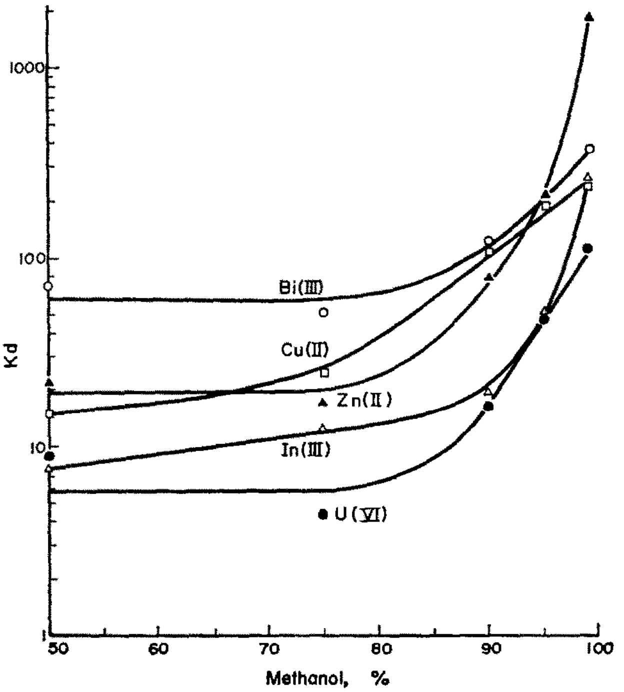


FIG. 1.—Distribution coefficients of metals on DEAE in methanol–1·1*M* NH_4SCN–0·52*M* HCl media as a function of methanol concentration.

TABLE II.—DISTRIBUTION COEFFICIENTS OF METALS ON DEAE IN METHANOL–NH_4SCN–HCl(19:1) MEDIA

Metal	[HCl], *M*	[NH_4SCN], *M*		
		0·11	1·1	3·2
Cu(II)	0·52	43	200	117
	0·11	124	190	119
	0·011	107	191	120
	0·0011	897	335	121
Zn	2·0	110	167	127
	0·52	460	208	111
	0·11	870	310	103
	0·011	1140	280	94
	0·0011	1080	339	95
Cd	2·0	497	250	114
	0·52	460	137	23
	0·011	30	14	3
In	0·52	35	53	69
	0·11	33	46	76
	0·011	56	63	53
	0·0011	32	55	48
Bi	2·0	856	400	300
	0·52	708	188	146
	0·11	528	190	152
	0·011	610	212	202
	0·0011	685	196	133
U(VI)	0·52	9	50	100
	0·11	40	55	84
	0·011	42	67	90
	0·0011	55	76	104

but the number of cations adsorbed is still much less than that of metals adsorbed on Dowex 1 from aqueous thiocyanate media[6,14] and from mixed solvent thiocyanate media.[15] Thus, the number of thiocyanato complexes adsorbed by the various ion-exchange systems involved is in the order: strongly basic anion-exchange resin–aqueous thiocyanate and mixed solvent thiocyanate media > DEAE–methanolic thiocyanate media > DEAE–aqueous thiocyanate media.

Figure 2 indicates the effect of loading on the distribution coefficients of Cu(II), Zn, Cd, In, Bi and U(VI) in methanol–thiocyanate–hydrochloric acid media (19:1).

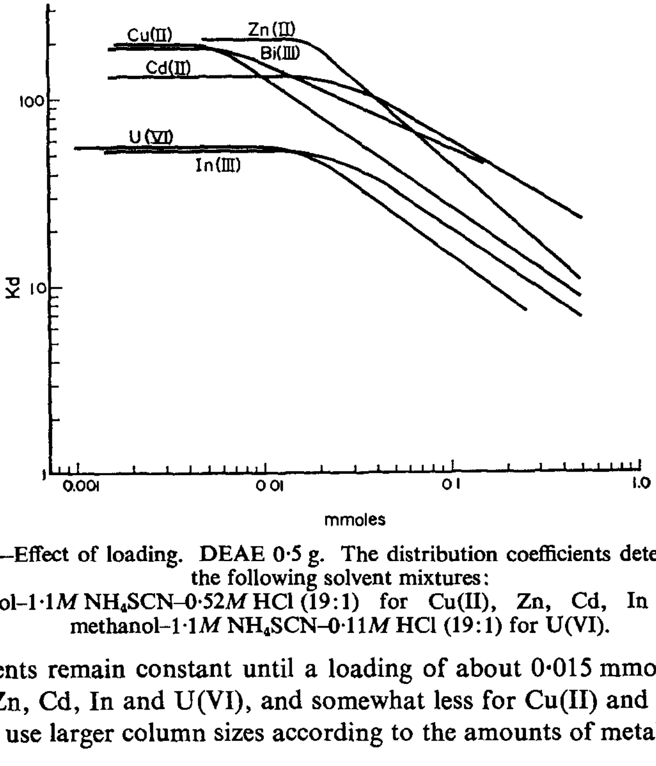


FIG. 2.—Effect of loading. DEAE 0·5 g. The distribution coefficients determined in the following solvent mixtures:
methanol–1·1M NH_4SCN–0·52M HCl (19:1) for Cu(II), Zn, Cd, In and Bi;
methanol–1·1M NH_4SCN–0·11M HCl (19:1) for U(VI).

The coefficients remain constant until a loading of about 0·015 mmole per 0·5 g of DEAE for Zn, Cd, In and U(VI), and somewhat less for Cu(II) and Bi. It may be necessary to use larger column sizes according to the amounts of metal to be loaded.

Separations

The adsorption of most other metals is sufficiently low to allow their separation on columns, and selectivity can still be achieved for the separation of the six metals (Table II) in this ion-exchange system.

Multicomponent separations were attempted and the results obtained are shown in Table III and Fig. 3. Each separation was repeated more than three times and averages and standard deviations are listed for the individual metals. Recoveries are satisfactory. In order to show the versatility of the present ion-exchange system, U(VI) and the mixed rare earths in proportions of 1:100 and 100:1 (runs 2 and 3) were separated from each other. A four-component chromatographic separation is illustrated in Fig. 3. The separation was quantitative and no marked tailing was found.

When cellulosic ion-exchangers are used in mixed solvents, they do not always exhibit their inherent ion-exchange function regardless of the nature of the organic solvent used. For solvent systems involving aprotic solvents a pronounced partition

TABLE III.—SEPARATIONS†

Run	Metals	Added, μg	Found, μg	No of detns.	Eluted with
1	Ni	50·5	$51{\cdot}2 \pm 2{\cdot}3_7$	3	15 ml of *a*
	Cu(II)	49·9	$49{\cdot}5 \pm 2{\cdot}3_8$	3	15 ml of *b*
	Zn	52·7	$52{\cdot}8 \pm 2{\cdot}3_8$	3	20 ml of *c*
2	Mixed R.E.*	$50{\cdot}0 \times 10^2$	$(50{\cdot}2 \pm 0{\cdot}2) \times 10^2$	3	25 ml of *d*
	U(VI)	46·5	47·3, 39·5, 46·0	3	20 ml of *e*
3	Mixed R.E.*	20·0	$20{\cdot}5 \pm 0{\cdot}3_8$	4	12 ml of *d*
	U(VI)	$28{\cdot}0 \times 10^2$	$(28{\cdot}4 \pm 0{\cdot}6_6) \times 10^2$	4	20 ml of *e*
4	Cd	$36{\cdot}7 \times 10^2$	$(36{\cdot}5 \pm 0{\cdot}0_7) \times 10^2$	3	55 ml of *f*
	In	54·0	$58{\cdot}7 \pm 1{\cdot}9_0$	3	20 ml of *e*
5	Ga	$111{\cdot}7 \times 10^2$	$107{\cdot}9 \times 10^2$, $107{\cdot}8 \times 10^2$, n.d.	3	25 ml of *f*
	In	54·0	$52{\cdot}8 \pm 2{\cdot}5_7$	3	20 ml of *e*
6	Al	$11{\cdot}1 \times 10^2$	$(11{\cdot}3 \pm 0{\cdot}1_8) \times 10^2$	4	25 ml of *g*
	In	54·0	$52{\cdot}6 \pm 1{\cdot}8_7$	4	20 ml of *e*

† Columns containing 1 g of DEAE used throughout.

* Equal amounts of Y(III), La(III) and Sm(III) contained.

Eluents used:

a: methanol–0·11*M* NH_4SCN/0·0011*M* HCl (19:1).
b: methanol–1·1*M* HCl (4:1).
c: 2·1*M* HCl.
d: methanol–1·1*M* NH_4SCN/0·11*M* HCl (19:1).
e: 1·1*M* HCl.
f: methanol–2·0*M* NH_4SCN/0·011*M* HCl (19:1).
g: methanol–2·0*M* NH_4SCN/0·52*M* HCl (19:1).

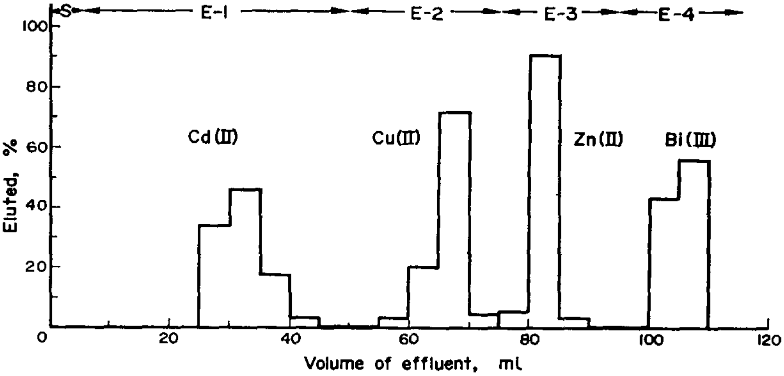


FIG. 3.—Chromatographic separation of Cd(II), Cu(II), Zn(II) and Bi(III).
S: sample solution—methanol-1·1*M* NH_4SCN–0·0011*M* HCl (19:1)
E-1: methanol-1·1*M* NH_4SCN–0·0011*M* HCl (19:1)
E-2: methanol-1·1*M* HCl (4:1)
E-3: methanol-1·1*M* HCl (1:1)
E-4: 2·1*M* HCl
Cd 54·8 μg added, 57·0 μg found; Cu(II) 100 μg added, 105 μg found; Zn 105 μg added, 110 μg found; Bi 212 μg added, 213 μg found.

mechanism appears to prevail, even though apparent adsorption takes place, as revealed in thin-layer chromatographic systems involving DEAE.[16,17] Therefore, a plain cellulosic support may retain metals in some cases.

In the present study it has been demonstrated that the addition of a protic solvent, methanol, to the thiocyanate-hydrochloric acid media permits more metals to be adsorbed on DEAE columns, thus extending the utility of DEAE in inorganic column chromatography.

Acknowledgement—The authors thank the Ministry of Education, Japan Government, for a grant-in-aid.

Zusammenfassung—Nur wenige Metalle können aus wäßrigen Thiocyanat-Chlorid-Medien an DEAE-Cellulose adsorbiert werden. Cu(II), Zn, Cd, In, Bi und U(VI) werden jedoch aus Gemischen von Methanol, Thiocyanat und Salzsäure verstärkt an DEAE-Cellulose adsorbiert. Die Verteilungskoeffizienten dieser Metalle werden in Abhängigkeit von den Konzentrationen an Methanol, Ammoniumthiocyanat und Salzsäure angegeben. Die Unterschiede in der Adsorption zwischen den Metallen ermöglichen viele nützliche Trennverfahren von Gemischen aus zwei, drei und vier Komponenten an kurzen Säulen mit 1–1,5 g DEAE-Cellulose.

Résumé—Seulement quelques métaux peuvent être adsorbés sur la DEAE-cellulose à partir de milieux aqueux thiocyanate-chlorure. Toutefois, plusieurs ions métalliques, comprenant Cu(II), Zn, Cd, In, Bi et U(VI), présentent une adsorption accrue sur la DEAE-cellulose à partir de mélanges méthanol-thiocyanate-acide chlorhydrique. Les coefficients de partage pour ces métaux sont donnés en fonction de la concentration en méthanol, thiocyanate d'ammonium et acide chlorhydrique. Des différences d'adsorption parmi les métaux permettent de nombreuses séparations utiles, comprenant celles de mélanges à deux, trois et quatre composants, sur des colonnes courtes contenant 1–1,5 g de DEAE-cellulose.

REFERENCES

1. R. Kuroda and N. Yoshikuni, *Talanta*, 1971, **18**, 1123.
2. R. A. A. Muzzarelli, *Advances in Chromatography*, Vol. 5, ed. J. C. Giddings and R. A. Keller, p. 127. Dekker, New York, 1968.
3. R. Kuroda, T. Kiriyama and K. Ishida, *Anal. Chim. Acta*, 1968, **40**, 305.
4. *Idem, ibid.*, 1968, **41**, 537.
5. R. Kuroda, T. Ono and K. Ishida, *Bunseki Kagaku*, 1971, **20**, 1142.
6. K. Kawabuchi, H. Hamaguchi and R. Kuroda, *J. Chromatog.*, 1965, **17**, 567.
7. Y. Shijo and T. Takeuchi, *Bunseki Kagaku*, 1965, **14**, 511.
8. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., pp. 443, 338. Interscience, New York, 1959.
9. R. M. Rush and J. H. Yoe, *Anal. Chem.*, 1954, **26**, 1354.
10. O. Kammori, *Bunseki Kagaku*, 1967, **16**, 142.
11. H. Onishi and Y. Toita, *ibid.*, 1965, **14**, 1141.
12. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 3rd ed., p. 353. Interscience, New York, 1959.
13. N. Ishiwatari, H. Nagai and Y. Toita, *Bunseki Kagaku*, 1963, **12**, 603.
14. A. K. Majumdar and B. K. Mitra, *Z. Anal. Chem.*, 1965, **208**, 1.
15. D. K. Pietrzyk and D. L. Kiser, *Anal. Chem.*, 1965, **37**, 1578.
16. R. Kuroda, N. Yoshikuni and K. Kawabuchi, *J. Chromatog.*, 1970, **47**, 453.
17. K. Oguma and R. Kuroda, *ibid.*, 1970, **52**, 339.

Talanta, 1972, Vol. 19, pp. 1049 to 1058. Pergamon Press. Printed in Northern Ireland

CANDOLUMINESCENCE—A NEW FLAME TECHNIQUE FOR TRACE ANALYSIS—I

DEVELOPMENT OF A METHOD FOR DETERMINATION OF BISMUTH

R. BELCHER, S. BOGDANSKI and A. TOWNSHEND
Chemistry Department, Birmingham University, P.O. Box 363, Birmingham B15 2TT, U.K.

(*Received* 6 *December* 1971. *Accepted* 11 *January* 1972)

Summary—Early work on candoluminescence is reviewed and the phenomenon is investigated experimentally for the elements Bi, Mn, Sb and the lanthanides. It is demonstrated that it is feasible to determine bismuth (5–1000 μg) by measuring its candoluminescent intensity at 399 nm, using a calcium hydroxide–calcium sulphate matrix and a hydrogen–helium–air flame.

CERTAIN metal oxides containing trace amounts of activating elements luminesce when placed at the outer edge of a hydrogen diffusion flame. The phenomenon was reported as early as 1842 by Balmain,[1] and was termed *candoluminescence* by Nichols[2] to distinguish it from thermal incandescence, cathodoluminescence and other types of luminescence. Donau[3] has used candoluminescence for qualitative analysis. He detected traces of bismuth and manganese by adding them to calcium carbonate and observing their respective characteristic blue and yellow emissions in the hydrogen flame. Von Neunhoeffer[4] extended this work to provide a qualitative test for a number of lanthanides in a calcium carbonate matrix.

Nichols and his co-workers[2] made a prolonged study of candoluminescence. They investigated numerous activators and matrices,[5] and showed that for many matrix–activator pairs there were particular flame-temperature limits within which luminescence was produced.[6] They also established that luminescence occurred only when the matrix was held at the outer edge of the hydrogen diffusion flame. Smith[7] published a review of developments in candoluminescence up to 1940 in which he clarified some of Nichols's work and presented spectrograms resulting from the presence of bismuth, manganese, lead and antimony in calcium oxide. The nature of candoluminescence remained obscure until Arthur and Townend[8] showed that it arose from a radical-recombination process. The high radical concentration in the outer layers of the hydrogen diffusion flame is thus the reason for the maximal candoluminescence of matrices placed in this region. Recent work by Sokolov and co-workers[9,10] on the mechanism of candoluminescence has confirmed the validity of the radical-recombination theory.

These previous investigations indicated that candoluminescence might provide a very sensitive means of quantitative inorganic analysis, especially for bismuth, lead, manganese and some lanthanides. Initial experiments were carried out by spraying a solution of a calcium salt, containing some bismuth, *via* a conventional flame photometric pneumatic nebulizer, into a hydrogen diffusion flame. No luminescence was observed, probably because the solid particles formed pass too quickly through the flame. All further experiments, therefore, were concerned with obtaining a reproducible luminescence from a solid calcium hydroxide matrix in a fixed position in the flame. Bismuth was chosen as the activator for these development studies because of its easily visible brilliant blue emission. Calcium hydroxide was preferred to calcium carbonate because luminescence was initiated more quickly.

It was found, in accord with the observations of earlier workers, that the most intense candoluminescence occurred when the calcium hydroxide surface was placed at the outer " edge" of the diffusion flame. However, the irregular motion of the flame in this region caused the luminescence to fluctuate greatly in intensity. Addition of nitrogen to the hydrogen made the flame more rigid, but restricted the most active, outer, zone of the flame to a very narrow region, so that it became impossible, with the apparatus used, to position the sample surface reproducibly in this zone. In a hydrogen or hydrogen–nitrogen diffusion flame, no luminescence was observed from a sample surface in the interior of the flame. Introduction of a small proportion of air into the hydrogen *via* the spray aperture of a conventional nebulizer operated by nitrogen, so that the flame temperature was well below 1000°, allowed candoluminescence to be produced in the flame interior. As the composition of the flame interior is less variable than that of the outer zone, accurate positioning of the calcium hydroxide surface became much less critical. However, the intensity of luminescence under these conditions was between 1/10 and 1/100 that produced at the edge of a pure hydrogen flame. This was thought to be due to the nitrogen reducing the incidence of radical recombination by collisional deactivation, and had been observed previously[8]. Replacement of nitrogen by helium, a much less effective quenching agent, gave appreciably enhanced luminescence emission, and was used in all subsequent experiments. No doubt argon would be as effective as helium.

EXPERIMENTAL

Apparatus

An Evans Electroselenium Ltd. (EEL) model 240 atomic-absorption spectrophotometer was operated in the emission mode (0·4 mm slit), with water-cooling device removed. The EEL emission burner with a circular 2·5 cm diameter head was used. Hydrogen was introduced *via* the fuel input system, helium *via* the support gas system, and additional oxygen was available from the secondary support gas system. All gases were mixed before entering the burner head. The spectrophotometer was modified to function, when required, as a scanning instrument, by coupling an electric motor to the wavelength fine-control drive.

The sample-holder assembly is shown in Fig. 1. The sample to be tested was inlayed onto a hexagonal aperture (max. diagonal 5 mm) in the head of a 3 cm long steel Allen screw (outside head diameter 8 mm). The screw was inserted into the accurately positioned bar, so that its head was reproducibly positioned in the flame in line with the optical system, 3·8 cm above the burner head. The screw head was tilted 5° to facilitate contact between the sample surface and the impinging flame.

Reagents

Calcium solution for matrix preparation. Analytical-reagent grade calcium carbonate dissolved in dilute nitric acid and diluted so that 1 g of calcium is contained in 4–10 ml of soln.

Activator solutions. A 10 mg/ml bismuth solution was prepared by dissolving $Bi(NO_3)_3 . 5H_2O$ in 1M nitric acid. A 250 ppm solution was prepared by appropriate dilution with water.

Praseodymium, dysprosium, samarium, neodymium, ytterbium and yttrium solutions were prepared from the acetates. Other lanthanide solutions were prepared by dissolution of the respective oxides, or in the case of erbium a metal ingot, in dilute nitric acid.

Preparation of sample, and measurement of candoluminescence

The calcium solution (containing 0·5 g of calcium) was added to a 30-ml test-tube, followed by the desired volume of activator solution (see below) and water to make up to 10 ml. Plaster of Paris ($CaSO_4 . \frac{1}{2}H_2O$, 1 g) was added, the test-tube was corked, and the mixture shaken well. An excess of 30% sodium hydroxide solution was added, the suspension was shaken for 5 min and filtered by suction on sintered glass until the precipitate had compacted to a dense cake. The solid was inlaid in a *clean* screw head so that the surface was flat and smooth, and the screw was placed in an oven at 105°

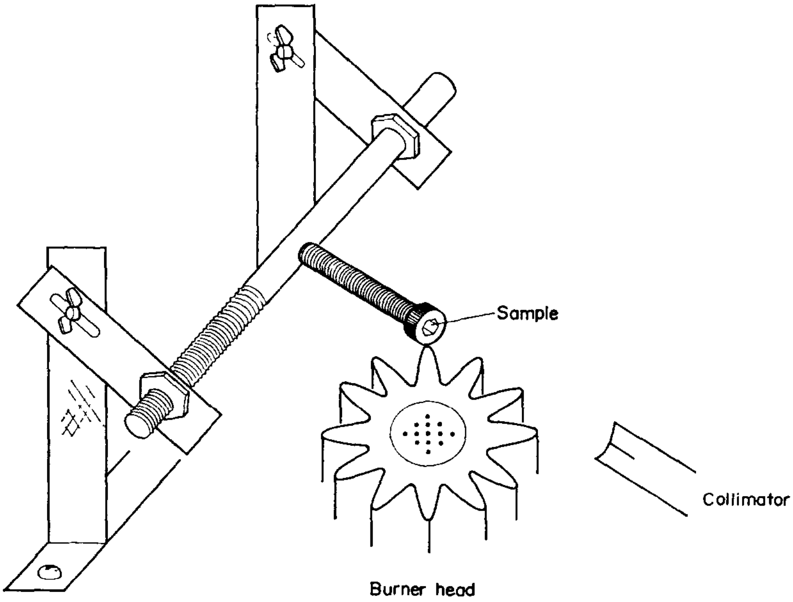


FIG. 1.—Burner and sample holder assembly.

for 15 min. Any excess of material around the inlay was removed, and the screw was inserted into its holder, in the desired position.

The helium was turned on (5·2 units on Brooks tube 4–65) followed by the hydrogen (3·1 units on Brooks tube 4–65) and the flame was ignited. The change in emission intensity with time was recorded on a chart-recorder. The screw was removed from the flame by rotating the bar and replaced by another screw which was then introduced into the flame by rotating the bar back again.

The bismuth-stimulated candoluminescence was measured at 399 nm. A calibration graph for bismuth was prepared by adding the following volumes of 250-ppm bismuth solution to the calcium solution: 20, 40, 60, 100, 300, 500, 700, 1000 and 2000 μl. The maximal intensity produced in each instance was used for the calibration.

The spectra from the various activators (Figs. 2–5) were recorded under the conditions outlined above, *except* that a 10-sec blast of air (4·65 units on Brooks tube 4–65) was introduced into the flame to activate the matrix (see later) before measurement of the candoluminescence.

RESULTS AND DISCUSSION

It quickly became apparent that there were several parameters that had to be recognized and controlled before reproducible luminescence could be achieved. Apart from the flame composition and position of the sample in the flame, which were readily optimized, it was the preparation and pretreatment of the sample that were the greatest problems. Although calcium hydroxide alone was a suitable matrix, inclusion of 50% of Plaster of Paris imparted more rigidity to the matrix and made it easier to produce a smooth surface. The amount of water retained in the matrix was also important. Too much water caused the matrix to shrink when heated in the oven, thus hindering the exposure of the surface to the flame. It was essential, also, to dry the matrix at the relatively low temperature of 105° to avoid forcing the matrix from the screw with a sudden pressure of water vapour. The drying time of 15 min was found to be optimal. Further drying often hampered the initiation of candoluminescence. The activator was introduced into the matrix by co-precipitation. Thus, it was necessary to standardize the conditions of precipitation of the matrix–activator mixture,

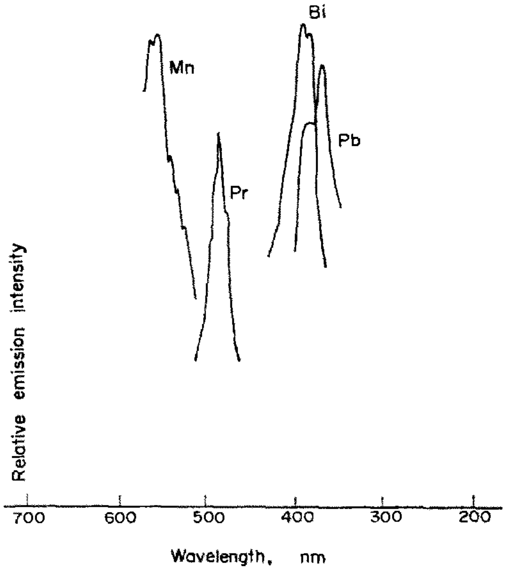


FIG. 2.—Candoluminescence emission peaks of manganese, praseodymium, bismuth and lead (background as spectrum A, Fig. 6).

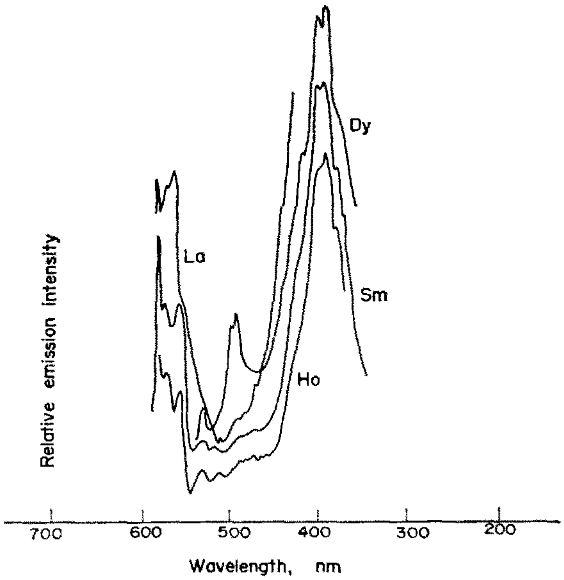


FIG. 3.—Candoluminescence spectra of lanthanum, dysprosium, samarium and holmium (background as spectrum B, Fig. 6).

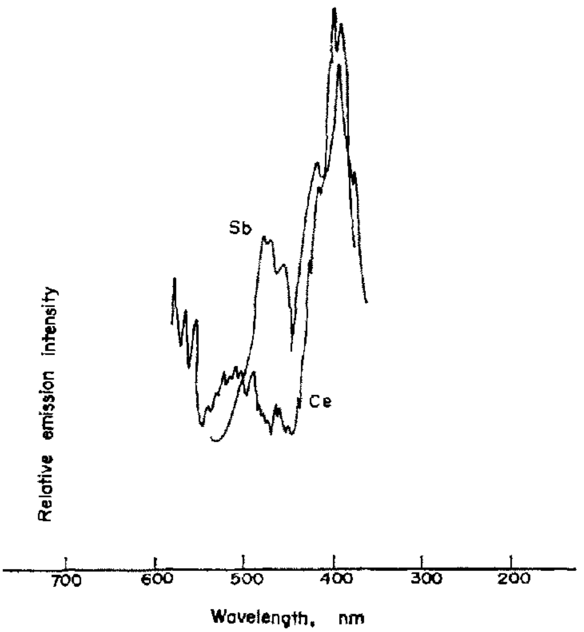


FIG. 4.—Candoluminescence spectra of cerium and antimony (background as spectrum B, Fig. 6).

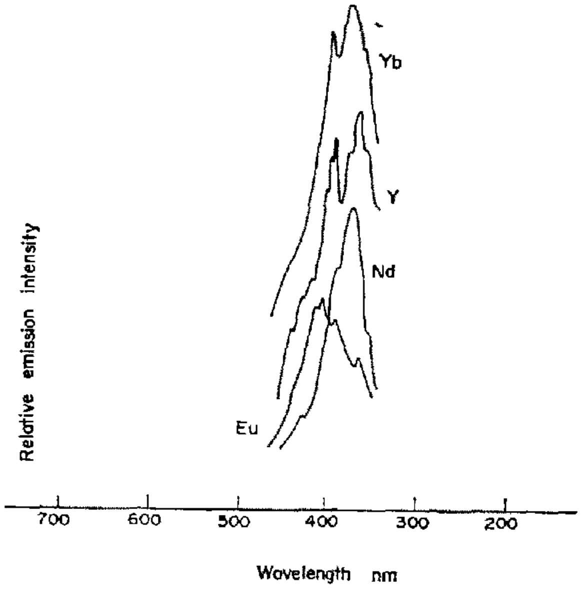


FIG. 5.—Candoluminescence peaks of europium, ytterbium, yttrium and neodymium (background as spectrum B, Fig. 6).

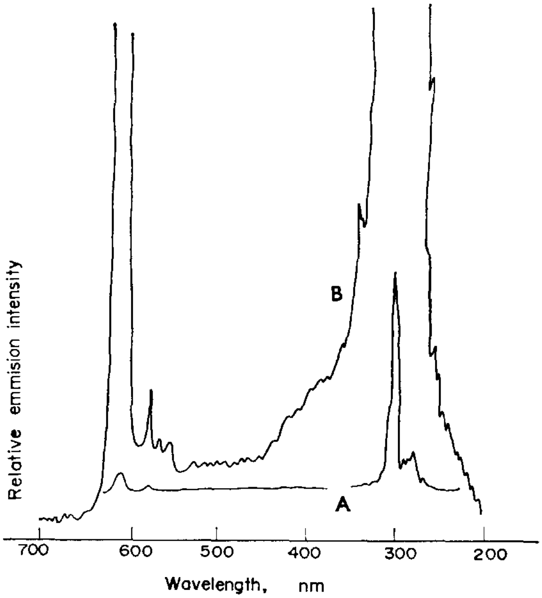


FIG. 6.—Background emission spectrum, with a helium-diluted flame. Spectrum A is recorded at 1/20 the sensitivity for spectrum B.

both to have reproducible activator inclusion in the matrix, and to produce a precipitate with reproducible water-retaining characteristics.

Purity of reagents and screw cleanliness were further sources of variable results. A commercial preparation of calcium hydroxide, laboratory-reagent grade calcium oxide, and calcium hydroxide prepared from laboratory-reagent grade calcium nitrate each gave a yellow luminescence in the absence of added activator, with a spectrum identical to that of manganese-activated candoluminescence (see Fig. 2). Thus it was necessary to prepare calcium hydroxide from analytical-reagent grade materials; such a matrix was free from the yellow luminescence, and gave a background as shown in Fig. 6. The screws required scrupulous cleaning to remove candoluminescent material. This involved scraping out most of the matrix, washing with dilute hydrochloric acid, followed by water and finally heating to red-heat in the hydrogen-added air flame.

Determination of bismuth

Figure 2 shows the candoluminescence spectrum of bismuth; the peak was at 399 nm. The change in intensity of the emission at this wavelength, measured under the recommended conditions, that occurs after ignition of the flame, is shown in Fig. 7. There was a constant time before light emission began which was independent of activator concentration. The shape of this emission–time curve could be changed, however, by altering the rate of air aspiration or by changing the position of the sample in the flame. Under constant flame conditions and with reproducible sample preparation technique, the maximal intensity of the emission at 399 nm was a function of the amount of bismuth added to the calcium solution. A log-log calibration graph was linear (Fig. 8). The vertical diameter of each spot represents the standard deviation calculated from 12 intensity measurements made on samples taken from one

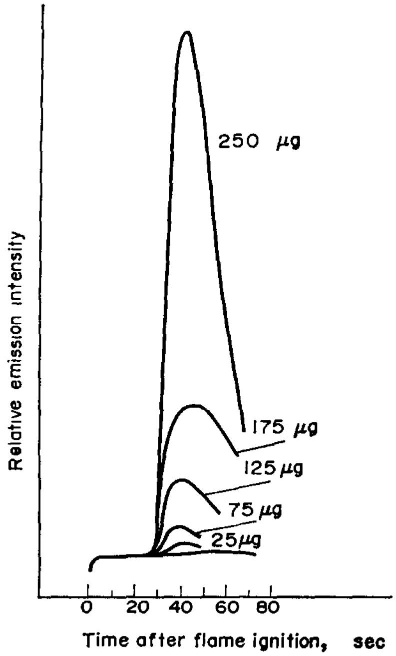


FIG. 7.—Variation in emission at 399 nm with time, for the amounts of bismuth shown.

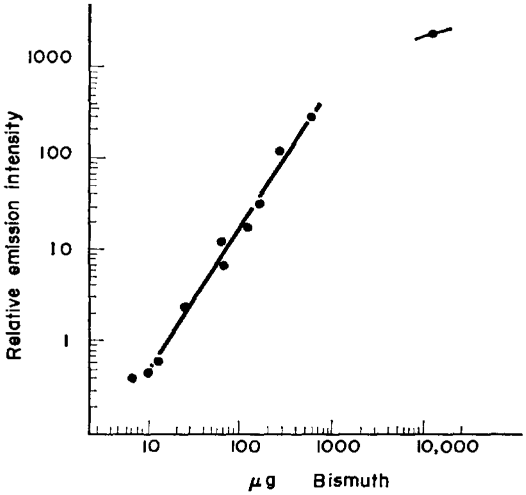


FIG. 8.—Variation of peak emission intensity at 399 nm with amount of bismuth.

calcium hydroxide precipitation. The coefficient of variation remains at *ca.* 10% over the whole range of bismuth concentrations studied. In order to achieve this precision with the apparatus used, it was necessary to work in diffuse light, to avoid variations in background illumination.

Figure 7 also shows the background spectrum in the absence of bismuth. The only emissions recorded, which were also present in the absence of the screw, were the OH band at 306 nm (and the second-order band at 612 nm) and a very faint emission at 589 nm, presumably arising from traces of sodium. The region between *ca.* 320 and 600 nm was thus free of significant background variation.

The present paper is intended to establish the feasibility of using candoluminescence as an analytical technique. It was possible, by using increased detector amplification, to detect as little as 0·5 μg of bismuth added to the original calcium solution. However, as only a small fraction of the calcium precipitate was used for one screw inlay, and as it is probably only the surface layers of the inlay that are involved in candoluminescence, the amount of bismuth actually being monitored is probably in the ng region. Investigations are continuing in order to achieve such increased sensitivity.

Effects of other activators

Previous workers have identified a number of activators, especially many of the lanthanides, that induce candoluminescence when present in a calcium hydroxide matrix. The candoluminescence of the following elements was measured by using the flame and sample preparation conditions optimized for bismuth: Mn, Fe, Ni, Pb, Y, Sb, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb. Of these, only iron, nickel, gadolinium and erbium gave no luminescence, although gadolinium gave a bright red luminescence when more air was added to the flame. The candoluminescence colours given by the other elements investigated are summarized in Table I, together with the wavelengths of the major candoluminescence peaks, and the colours observed by Donau,[3] Smith[7] and von Neunhoeffer.[4] Observations by Nichols are not included because many of his "pure" matrices were also observed to luminesce. Apart from the colours of lanthanum and samarium, the present observations agree with those of previous workers.

The candoluminescence spectra of the elements investigated are shown in Figs. 2–5. The spectrograms of lead, bismuth, manganese, antimony and praseodymium, as measured by Smith,[7] agree closely with the present spectra. Manganese, lead, bismuth and praseodymium each gave only one emission band, although praseodymium must have had another peak at a wavelength greater than that of the peak observed but not picked up by the photodetector system used, because the luminescence was red. The praseodymium spectrogram given by Smith[7] shows an additional peak at 600 nm, which would have been obscured in the present instance by the second-order diffraction of the 306 nm OH band. Samarium, lanthanum and holmium gave almost identical spectra, and that of dysprosium differed from these only in the presence of additional peaks at 490 and 530 nm (Fig. 3). Cerium and antimony (Fig. 4) gave intense, complex spectra, whereas neodymium, yttrium, ytterbium and europium all gave multiple peaks in the 400 nm region.

It is interesting that although individual elements gave rise to characteristic candoluminescence spectra, those spectra usually consisted of one or more peaks occurring in three spectral regions, *viz.* ~400, 500 and 570 nm. Only manganese was an exception, with a single emission peak at 600 nm. Thus, although a number of spectral bands may be resolved from each other, as in the case of manganese and bismuth, the grouping of emission peaks limits the possibilities of resolving the spectral peaks of different elements, and thus restricts the selectivity of the technique. However, other possibilities exist for improving selectivity. Although a detailed investigation of interference effects has not yet been made, it was apparent that appreciable differentiation

TABLE I.—CANDOLUMINESCENCE GIVEN BY VARIOUS ACTIVATORS

Activator	Peak maxima, *nm*	Emission colour (intensity)	Previously observed colour
Mn	568	yellow (v.s.)	yellow
Y	387,360	blue-violet (s)	blue-violet
Sb	390,480	green-blue (v.s.)	blue-green
La	400,395,568	white-yellow (s)	brick red
Ce	395,500,568	green (s)	yellow-green
Pr	490	red (v.s.)	red
Nd	368	?(v.wk.)	orange red
Sm	400,395,(568)	bluish (wk)	yellow-green
Eu	403	? (v.wk)	—
Dy	400,390,490,530	green (wk)	pale green
Ho	390	? (v.wk)	—
Yb	390,370	blue-violet (m)	—
Pb	368	blue (m)	blue
Bi	400	blue (v.s.)	blue
Tb	—	—	yellow green

v.s. = very strong
s = strong
m = medium
wk = weak
v.wk. = very weak

between elements with similar candoluminescence spectra could be made by changing the flame conditions. The spectra in Figs. 2–5 were all measured *after* the sample had been pretreated in a hydrogen–helium flame into which a 10-sec blast of of air had been injected. Without this pretreatment, praseodymium and a number of other elements did not give rise to luminescence, whereas bismuth still gave an intense emission, as shown by the analytical procedure for bismuth, which does not involve pretreatment in the flame. An increase in the permanent amount of air introduced into the flame caused the 400-nm peaks of dysprosium and cerium to disappear, although the red emission from gadolinium now became apparent. Bismuth still responded well in the presence of extra air, although the time–luminescence response (Fig. 7) was markedly changed. These phenomena are a consequence of the different flame conditions (temperature, radical concentrations, *etc*) required to produce candoluminescence in the presence of different activators. Thus, judicious choice of flame conditions could lead to appreciable differentiation between activators, although precise control would be essential for quantitative analytical measurements.

Conclusion

Candoluminescence has been shown to be a sensitive and potentially useful technique for the determination of bismuth. It is expected that much greater sensitivity will be achieved as the technique is developed and refined. At present, the sample preparation involves co-precipitation of bismuth with the calcium hydroxide used in the matrix. This is time-consuming and wasteful of sample, and methods of direct introduction of bismuth into the inlaid matrix would be preferable and give much greater analytical sensitivity. Methods for achieving this are being investigated.

The technique also appears to provide a sensitive means of determining many of the lanthanides, as well as manganese, antimony and lead. A detailed examination of these elements is in progress.

Zusammenfassung—Es wird eine Übersicht über frühe Arbeiten auf dem Gebiet der Candolumineszenz (Lumineszenz über 1000°C erhitzter Stoffe) gegeben und das Phänomen an den Elementen Bi, Mn, Sb und den Lanthaniden experimentell untersucht. Es wird gezeigt, daß man Wismut (5–1000 μg) durch Messung seiner Candolumineszenz-Intensität bei 399 nm bestimmen kann. Man verwendet eine Calciumhydroxid-Calciumsulfat-Matrix und eine Wasserstoff–Helium–Luft-Flamme.

Résumé—On passe en revue les travaux anciens sur la candoluminescence et l'on étudie le phénomène expérimentalement pour les éléments Bi, Mn, Sb et les lanthanides. On démontre qu'il est possible de doser le bismuth (5–1000 μg) en mesurant son intensité candoluminescente à 399 nm, en utilisant une matrice hydroxyde de calcium–sulfate de calcium et une flamme hydrogène–hélium–air.

REFERENCES

1. W. H. Balmain, *Phil. Mag.*, 1842, **21**, 270.
2. E. L. Nichols, H. L. Howes and D. T. Wilber, *Carnegie Inst. Publn.* No. 348, 1928.
3. J. Donau, *Monatsh.*, 1913, **34**, 949.
4. A. von Neunhoeffer, *Z. Anal. Chem.* 1951, **132**, 91.
5. E. L. Nichols and L. J. Boardman, *J. Opt. Soc. Amer.*, 1930, **20**, 115.
6. E. L. Nichols and H. L. Howes, *ibid.*, 1932, **22**, 170.
7. E. C. W. Smith, *Inst. Gas Engineers*, 1940, **90**, 519.
8. J. R. Arthur and D. T. A. Townend, *Nat. Bur. Stds. Circular* 532, p. 99 (1954).
9. Th. Wolkenstein, V. A. Sokolov, A. N. Gozbau and V. G. Kornich, *Proc. Intern. Conf. Luminescence*, 1966, **2**, 1433.
10. A. I. Bazhin, V. V. Styrov and V. A. Sokolov, *Russ. J. Phys. Chem.*, 1970, **44**, 107.

Talanta, 1972, Vol. 19, pp. 1059 to 1065. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF SUBNANOGRAM AMOUNTS OF CHROMIUM IN DIFFERENT MATRICES BY FLAMELESS ATOMIC-ABSORPTION SPECTROSCOPY

G. TESSARI and G. TORSI
Istituto di Chimica Analitica, Universita' di Bari, 173 Via G. Amendola,
70126 Bari, Italy

(*Received* 3 *November* 1971 *Accepted* 27 *December* 1971)

Summary—A carbon rod flameless atomizer is used for the determination of Cr in water, sea-water, sugar, glycine and blood. The reported analytical curves show that the quantitative determination of Cr in these matrices is feasible in the ppM–ppm range. The influence of the most common anionic and cationic interferents is reported.

SEVERAL methods for the determination of traces of chromium in different matrices have been investigated by a number of workers. In Table I some results from recent papers are gathered.[1–12] No attempt at a critical evaluation of these results has been made, but a rapid survey shows that ppM sensitivity can be reached with several techniques, sometimes with the help of a prior extraction.

Determinations of a number of elements at this impurity level are demanded by modern clinical analysis and by pollution control or environmental studies. The sensitivity is not the only demand made by these fields: further requirements are small size of sample (clinical analysis), freedom from interference by major constituents, and simplicity and rapidity (for possible automation or field application in environmental studies). In our opinion flameless atomic-absorption spectroscopy is a good candidate to fill these requirements, as is evident from the increasing literature in this field. Whereas for the L'vov furnace some conclusive results are reported,[9,13–27] there is a paucity of analytical data for the simpler West-type carbon rod, especially for the less volatile elements, in matrices other than water solutions.

In this study we have tried to assess the possibility of using the carbon rod atomizer for determination of subnanogram amounts of chromium, stressing more the aspect of interference effects in actual matrices than further improvement of the detection limit, on which other work is in progress in this laboratory.

EXPERIMENTAL

Reagents

All chemicals used were of analytical grade purity. Stock solutions were prepared with demineralized water and stored in polyethylene bottles. The chromium solutions were standardized by EDTA titration. The most dilute solutions were freshly prepared before use. In order to avoid erratic effects due to hydrolysis of Cr(III) followed by precipitation, the solutions were acidified to pH 1.

The argon used was certified to contain $<0{\cdot}1$ ppm *v*/*v* of oxygen and <5 ppm *v*/*v* of water. The hydrogen was certified to contain <5 ppm *v*/*v* of oxygen and <5 ppm *v*/*v* of water. At the beginning the gases were freed from oxygen and water by flowing them through two towers filled with pellets of a copper-based catalyst (BASF-Germany) kept at 150°. Since no improvement in the strength of the signal was found this purification was discontinued.

Apparatus

The instrumentation has already been described.[27] Some minor modifications were introduced into the flameless atomizer: (a) the rod supports were water-cooled; (*b*) the material chosen for the

TABLE I.—REPORTED RELATIVE AND ABSOLUTE DETECTION LIMITS FOR CHROMIUM WITH DIFFERENT ANALYTICAL TECHNIQUES

Technique	Relative detection limit	Absolute detection limit	Matrix	Experimental conditions	Remarks	Ref.
Neutron activation analysis	Sub ppM range		blood	8×10^{17} neutron/cm^2/sec; 5–6 weeks of cooling time after irradiation	high neutron flux	1
		0·45 μg	—	$4{\cdot}3 \times 10^{12}$ neutron/cm^2/sec; Short cooling time after irradiation	Medium neutron flux	2
Mass spectrometry		sub-pg range	pure compounds in pentane solutions	Direct insertion to the ionizing source, of vapour of fluorinated β-diketone Cr complexes		3
Gas chromatography	5 ppM	pg range	blood	After chelation with fluorinated diketones, the extracted chromium is detected by GLC		4
Atomic flame absorption spectroscopy	2 ppM		water solution	Air–acetylene premixed flame, infrared-heated spray chamber water cooled condenser, 102 × 0·56 mm double slot burner		5
Atomic flame emission spectroscopy	5 ppM		water solution	Nitrous oxide–acetylene premixed flame, 50 × 0·5 mm slot burner; determined in presence of high KCl concentration		6
Plasma emission	1 ppM		water solution	Induction-coupled high-frequency argon plasma		7
Arc emission (d.c.)	5 ppM		biological materials	Low pressure argon-stabilized d.c. arc	Concentration required for a 30% increase of the line over back-ground	8
L'vov type flameless atomizer		2 pg	water solution	Cuvette diameter 2·5 mm, argon pressure 2 atm, T = 2200°, atomic absorption	Amount corresponding to 1% absorption	9
Carbon rod flameless atomizer	1 ppM	5 pg	water solution, sea-water	2 × 2 × 15 mm carbon rod, argon pressure 1 atm, T ~ 3000°, atomic absorption		this work
Coulometric titrimetry		ng–μg range	water solution	Reduction of Cr(VI) with electrogenerated Fe(II)		10
Catalytic kinetics	1 ppM		water solution	Catalytic effect of Cr on the decomposition of Na amalgam		11
Luminescence analysis	0·1 ppM		water solution	Fluorescence at low temperature of Bu_3PO_4 extracts of Cr(III) thiocyanate complexes		12

rod was vitreous carbon, since it gives less interference at the highest temperatures.* The rod had a small cavity 1 × 1 × 2 mm at the centre. Temperatures up to 1600° were determined with a Pt(Pt, Rh 10%) thermocouple. Higher temperatures were evaluated by melting different metals in the form of thin strips wrapped around the rod. The highest temperature used was about 3000°. A step-down transformer was used with maximum output 30 V and 100 A. At variance with the previous report,[27] in this work steeper impulse signals were realized (rise-time 50 msec as measured on the oscilloscope so that the rise-time of 0·5–0·6 sec as read at the recorder was practically the overall time-response of the detector–amplifier–recording system. The maximum absorbance was measured on the plot of absorbance *vs.* time.

The flow-meters were calibrated according to the gas used. The sample (usually 1 or 2·5 μl) was injected with a micrometer syringe fitted with a polyethylene needle.

RESULTS AND DISCUSSION

Experimental parameters

The experimental conditions used in order to obtain the maximum signal were as follows.

(*a*) The 357·87 nm line was used (the sensitivity of the 359·35 nm line was 30% lower, at variance with the results reported[28] for flame AAS).

(*b*) Slit-width of 0·05 mm, corresponding to a band pass of 0·25 nm.

(*c*) A carrier gas flow-rate of 1 1./min was found the most convenient.

(*d*) Argon gave the best result as carrier gas. Hydrogen had a depressant effect on the signal, when flowing in the cell during the thermal "flash". The effect of hydrogen apparently could not be ascribed to a cooling of the rod surface, since increase of the input power did not restore the signal found in presence of argon.

(*e*) Owing to the dynamic character of the process of atomization the maximum temperature reported above (3000°) does not represent an average temperature of vaporization of chromium atoms but only the final temperature of the rod at the end of the thermal "flash". In this connection it is not so important to define the highest temperature experienced by the rod as to produce at the surface of the rod a variation of temperature fast enough to yield as compact as possible a burst of atoms, keeping in mind that the strength of the signal is also limited by the overall response of the detector–amplifier–recorder system. Practically every time a new rod was used, other conditions being equal, the optimum value of the voltage for the thermal flash was checked. Because of the similar dimensions of the rods used, this operation was not particularly time-consuming.

Procedure

As previously found, a gentle heating at a temperature below 100° in order to dry the sample is important to the final result. For the simplest aqueous solutions of chromium, it does not matter if a thermal treatment precedes the thermal flash or not; in any case a signal of the same strength is obtained and the analytical curves are practically the same. In the case of matrices containing interferent species, however, we have found that it is useful for the suppression of these interferences, or at least for minimizing them, to ash the sample at a temperature of 800–850° with only hydrogen gas flowing (at a rate of about 0·2 1./min). After this step the flowing gas is switched from hydrogen to argon at 1 1./min and the sample is flash-heated.

---

* An evaluation of the different carbon materials used for the rod will be published elsewhere.

TABLE II

Concentration of chromium, *ppM*	Volume, *μl*	No. of samples	Relative standard deviation, %
2000	1	20	3·7
800	1	20	5·0
200	1	20	7·0
40	1	20	9·3
10	1	20	17
2	5	18	18

Analytical curves and detection limits

Chromium in water gives a calibration curve which in a log/log plot is linear from 10^{-11} to 10^{-9} g, and then tails off. The same curve is obtained with $Cr(NO_3)_3$, Na_2CrO_4 and $Cr(SO_4)_3$. All these salts decompose[29–31] to give Cr_2O_3, a fairly stable oxide which is practically not reduced by hydrogen at temperatures up to 1300°.[32] Carbon is able to convert Cr_2O_3 into carbide at 1100°,[33,34] but it is doubtful if this can be a convenient route to Cr atoms, since there is the possibility of losing atoms of the analyte by evaporation, as suggested by the lowering of the strength of the signal when ashing at such a high temperature. $CrCl_3$ also gives the same calibration curve, but some care must be exercised to control the temperature during the ashing step, because this compound is much more volatile[35] than Cr_2O_3.

Since this technique makes use of a discrete sample, the response depends on the amount of sample, and accordingly in the calibration curve amounts and not concentrations are used.

In Table II relative standard deviations are reported in terms of chromium concentration, the volumes used also being quoted. From the relative standard deviation of 18% for 10^{-11} g of chromium (signal to noise, S/N, ratio about 5) it is estimated that, assuming $S/N = 2$, the absolute detection limit is approximately 5×10^{-12} g. On the usual 1% absorption basis, the sensitivity was 10^{-11} g.

As far as the relative detection limit is concerned, increasingly lower concentrations could in principle be detected if increasing volumes of sample were used. From a practical point of view volumes in excess of 5–10 μl are not convenient with our rod, and this sets 1 ppM as the relative detection limit, if it is necessary or desired to vaporize a single injection of sample. If the process of injecting and drying the sample is repeated many times, larger equivalent volumes are used and the concentration limit will be lowered. With this technique, using up to 50-μl volumes, we found $0{\cdot}4 \pm 0{\cdot}1$ ppM of chromium in the drinking water of the town of Bari (June 1971). However in presence of a concentrated matrix this process is impractical, owing to the deleterious effect, on the signal, of the concomitant increase of the interfering species.

Anionic and cationic interferences

Figure 1 shows the effect of some sodium salts of different anions on the signal strength of 80 ppM of chromium, from Na_2CrO_4, the volume of the solutions being 2·5 μl. Two patterns are recognizable in this plot. In the first, no practical interference is noted provided the concentrations of the various salts are kept in the ranges indicated in the figure. NaCl, $NaClO_4$ and $NaNO_3$ have in common this behaviour, which should be related to the ability of these salts to decompose and/or to vaporize

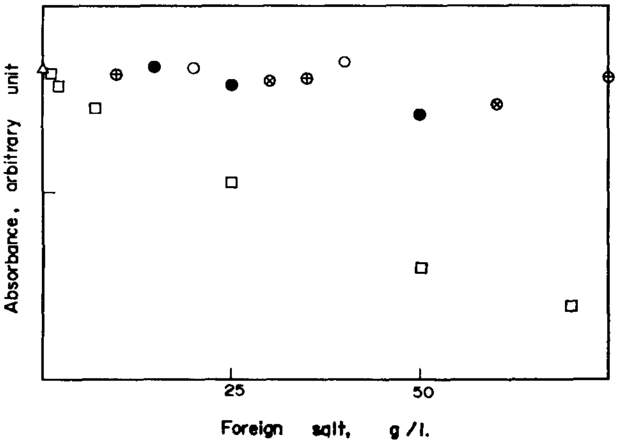


FIG. 1.—Optical response at 357·87 nm of 0·2 ng of Cr in water, as a function of the amounts of different Na salts added. △ Cr alone; □ Cr + Na_2HPO_4; ○ Cr + Na_2SO_4; ⊕ Cr + NaCl; ● Cr + $NaNO_3$; ⊗ Cr + $NaClO_4$.

at temperatures below the 800° used in the ashing step, leaving on the rod a sample with a much simpler matrix. (No hydrogen gas should be permitted to flow during the thermal decomposition of perchlorate matrices, since some chromium is observed to be locally vaporized in small plumes and the strength of the signal is accordingly lowered.) When $NaNO_3$ is present, the sample has a tendency to creep out of the notch during the decomposition process even when the temperature of the rod is carefully controlled. This has a negative effect on the signal, probably because the distribution of the sample over a larger area of the rod causes a less compact burst of atoms during the vaporization, owing to the thermal gradients along the rod. For a 2·5-μl sample this effect becomes evident at a sodium nitrate concentration of 50 g/l.

Sodium sulphate, thermally stable under the conditions of the ashing step, also gives no interference provided its concentration does not exceed 40 g/l. For concentrations of sodium sulphate greater than this, at the thermal flash the spray of material from the matrix becomes thick enough to give a scattering signal which simulates the presence of chromium. Disodium hydrogen phosphate at concentrations greater than about 5 g/l. lowers the chromium signal. We cannot say at the moment whether this effect is physical or chemical in nature and further study is necessary to elucidate the mechanism.

For investigation of cationic interferences, silver, nickel, cobalt and iron nitrates and potassium permanganate were used in 1000-fold ratio to chromium (as Na_2CrO_4). The chromium concentration was 80 ppM in a 2·5-μl sample. As mentioned above the presence of hydrogen during the ashing step at 800° is important when the matrix contains a large excess of these cations (except silver), since otherwise a smaller signal and sometimes no signal at all is obtained. As shown in Table III, Ag, Ni, Mn have practically no effect whereas, even with use of hydrogen, Co and Fe cause a loss of 30 % of the chromium signal.

More work is necessary to explain these results; all we can say is that the amount of oxygen in the sample after the ashing step appears an important parameter, possibly because it can increase the chance of recombination to chromium oxide after the flash.

TABLE III.—CATIONIC INTERFERENCES FOR CARBON ROD ATOMIZER

Ratio (interferent)/(Cr)	Signal strength %				
	$AgNO_3$	$Ni(NO_3)_2$	$KMnO_4$	$Co(NO_3)_3$	$Fe(NO_3)_3$
1000	101	98	102	70	70
200				80	83
100				101	90

Interferences from organic matrices

In order to investigate the effect of organic materials, chromium as Na_2CrO_4 was added to concentrated solutions of sugar and glycine. No interference was detected from concentrations of sugar or glycine up to 100 g/l., for 2·5 μl of 80-ppM chromium solution.

Calibration curve for chromium in sea-water

Some difficulties were experienced in the determination of chromium in sea-water since Cr(VI) is reduced in this matrix and the species then present, chromium chloride, is partially vaporized during the ashing step, unless extreme care is taken to control the temperature in order to vaporize NaCl, keeping at the minimum the loss of $CrCl_3$. In fact, even when this fractional vaporization was exploited, a large scatter of results was obtained. Attempts to transform $CrCl_3$ into a less volatile species and to simplify the matrix by displacing chloride with concentrated sulphuric acid were unsuccessful. In spite of the removal of excess of sulphuric acid during the ashing step large signals resulted which were more related to the modified matrix than to the amount of chromium in the sample. The formation of a chromium–EDTA complex and its thermal decomposition was the procedure finally used to obtain the analytical calibration curve.

The sea-water samples (taken from the shore near Monopoli, Bari, July 1971) with known amounts $CrCl_3$ added, were boiled with 0·1% EDTA solution for a few minutes, and then treated as already described. The means of results of five determinations on 2·5-μl samples fell on a straight line with the same slope as the curve obtained with standards prepared in pure water. From the plot a Cr concentration of 2 ± 1 ppM was obtained for the sample of sea-water.

Determination of chromium in blood

The blood was diluted 1:1 with water or with $Cr(NO)_3$ solutions in order to obtain blood samples with different chromium concentrations. Volumes of 1 μl of each sample were slowly preheated under hydrogen gas in order to remove the organic material without mechanical loss. The ashing step at 800° was retained and the gas flow switched from hydrogen to argon before the thermal flash*. The means of five determinations at each concentration gave a linear plot, from which a chromium concentration of 15 ppM was estimated for the pure blood sample. This value is slightly lower than that reported as normal by Metz[36](20–50 ppM) and was independently confirmed on a solution obtained by acid digestion of a 10-ml sample of the same blood at 200° for 1 hr.

---

* A carbon residue on the rod was removed mechanically after every ten runs.

Conclusions

The simplicity, speed in collecting analytical results, and the freedom—at least for the matrices investigated—from major interferences make this technique attractive for the determination of total content of chromium traces.

Acknowledgement—We thank Mr. V. Sacchetti and Mr. S. Giodice for co-operative help in the design and construction of the atomizer. Partial financial support from Consiglio Nazionale delle Ricerche is fully acknowledged.

Zusammenfassung—Zur Bestimmung von Cr in Wasser, Meerwasser, Zucker, Glycin und Blut wird ein Kohlestab als flammenloser Atomerzeuger verwendet. Die mitgeteilten analytischen Kurven zeigen, daß die quantitative Bestimmung von Cr in diesen Materialien im ppM–ppm-Bereich möglich ist. Der Einfluß der häufigsten anionischen und kationischen Störquellen wird mitgeteilt.

Résumé—On utilise un atomiseur sans flamme à tige de carbonne pour le dosage de Cr dans l'eau, l'eau de mer, le sucre, le glycocolle et le sang. Les courbes analytiques présentées montrent que le dosage quantitatif de Cr dans ces matrices est réalisable dans le domaine ppM–ppm. On rapporte l'influence des agents gênants anioniques et cationiques les plus communs.

REFERENCES

1. W. A. Haller, R. H. Filby and L. A. Rancitelli, *Nucl. Appl.*, 1969, **6**, 365.
2. H. P. Yule, *Anal. Chem.*, 1965, **37**, 129.
3. B. R. Kowalski, T. L. Isenhour and R. E. Sievers, *ibid*, 1969, **41**, 998.
4. L. C. Hansen, W. G. Scribner, T. W. Gilbert and R. E. Sievers, *ibid*, 1971, **43**, 349.
5. A. Hell, W. F. Ulrich, N. Shifrin and J. Ramirez-Muñoz, *Appl. Optics*, 1968, **7**, 1317.
6. E. E. Pickett and S. R. Koirtyohann, *Spectrochim. Acta*, 1968, **23B**, 235.
7. G. W. Dickinson and V. A. Fassel, *Anal. Chem.*, 1969, **41**, 1021.
8. K. M. Hambridge, *ibid.*, 1971, **43**, 103.
9. B. V. L'vov, *Atomic Absorption Spectrochemical Analysis*, English Edition, Hilger, London, 1970.
10. C. E. Champion, G. Marinenko, J. K. Taylor and W. E. Schmidt, *Anal. Chem.*, 1970, **42**, 1210.
11. G. I. Volkov and S. A. Mel'nikova, *Zh. Analit. Khim.*, 1970, **25**, 2049.
12. E. A. Solov'ev, E. A. Bozhevol'nov, A. I. Sukhanovskaya, G. P. Tikhonov and Yu. V. Golubev, *ibid.*, 1970, **25**, 1342.
13. B. V. L'vov, *Spectrochim. Acta*, 1961, **17**, 761.
14. H. Brandenberger and H. Bader, *Helv. Chim. Acta*, 1967, **50**, 1409.
15. H. Brandenberger, *Chimia*, 1968, **22**, 449.
16. H. Brandenberger and H. Bader, *At. Absorption News letter*, 1968, **7**, 53.
17. H. Massmann, *Spectrochim. Acta*, 1968, **23B**, 215.
18. R. Woodriff and R. W. Stone, *Appl. Optics*, 1968, **7**, 1337.
19. R. Woodriff and G. Ramelow, *Spectrochim. Acta*, 1968, **23B**, 665.
20. T. S. West and X. K. Williams, *Anal. Chim. Acta*, 1969, **45**, 27.
21. M. P. Bratzel, Jr., R. M. Dagnall and J. D. Winefordner, *ibid.*, 1969, **48**, 197.
22. R. G. Anderson, I. S. Maines and T. S. West, *Ibid.*, 1970, **51**, 355.
23. J. F. Alder and T. S. West, *ibid.*, 1970, **51**, 365.
24. M. D. Amos, *Amer. Lab.*, 1970 (August), 33.
25. H. M. Donega and T. E. Burgess, *Anal. Chem.*, 1970, **42**, 1521.
26. M. D. Amos, P. A. Bennet, K. G. Brodie, P. W. Y. Lung and J. P. Matoušek, *ibid.*, 1971, **43**, 211.
27. S. Dipierro and G. Tessari, *Talanta*, 1971, **18**, 707.
28. W. Slavin, *Atomic Absorption Spectroscopy*, p. 96. Interscience, London, 1968.
29. J. Cueilleron and O. Hartmanshenn, *Bull. Soc. Chim. France*, 1959, 168.
30. A. M. Sirina, I. I. Kalinichenko and A. I. Purtov, *Zh. Neorgan. Khim.*, 1970, **15**, 2430.
31. E. B. Singh and P. Sinha, *J. Indian Chem. Soc.*, 1970, **47**, 498.
32. V. G. Manchinskii, A. P. Lyuban and A. M. Semenov, *Nauchn. Tekhn. Inform. Byul. Leningr. Politekhn. Inst.*, 1961, 92.
33. K. Tonomura, S. Nishimura and Y. Kondo, *Suiyokwai-Shi*, 1966, **15**, 502.
34. W. L. Hunter and D. L. Paulson, *U.S. Bur. Mines, Rept. Invest.*, No 6755, 1966.
35. V. V. Pechkovskii, S. A. Amirova, N. I. Vorob'ev and T' V. Ostrovkaya, *Zh. Neorgan. Khim.* 1964, **9**, 2059.
36. W. Mertz, *Physiol. Rev.*, 1969, **49**, 163.

Talanta, 1972, Vol. 19, pp. 1067 to 1077. Pergamon Press. Printed in Northern Ireland

THE DEPENDENCE OF THE DROPPING MERCURY ELECTRODE POTENTIAL AT CONSTANT CURRENT ON THE CONCENTRATION OF AN ELECTROACTIVE CONSTITUENT INVOLVED IN REVERSIBLE OR IRREVERSIBLE ELECTRODE REACTIONS

YECHESKEL ISRAEL
IMI Institute for Research and Development, P.O. Box 313, Haifa, Israel

(*Received* 3 *September* 1971 *Accepted* 7 *January* 1972)

Summary—A new method is described in which the potential of the d.m.e. is measured as a function of the concentration of an electroactive constituent when a constant current is maintained by adjusting the voltage applied to the polarographic cell. Equations are derived describing the expected potential change caused by changing the concentration of a constituent involved in a reversible or an irreversible electrode reaction. Graphical interpretations of the derived equation are made, indicating the most suitable conditions for performing potential measurements, yielding potential differences that greatly exceed those obtained by conventional potentiometry, especially when the method is applied to irreversible electrode reactions at the d.m.e. Experimental evidence is presented, which not only verifies all expectations, but also indicates that the method offers a new approach to the investigation of some fundamental problems.

THE POTENTIAL of the dropping mercury electrode, d.m.e., depends on the concentration of a pure electroactive constituent in solution, when a constant current, lower than the diffusion current, is maintained by imposing suitable values of the applied voltage to the polarographic cell. It was reported earlier that for mercury(II) solutions the applied voltage required to maintain a constant current, depended on the concentration of mercury(II), in the range 10^{-6}–10^{-5} M, but did not account for the theoretical background of such a correlation.[1]

Figure 1 illustrates this dependence. Each of the lines A–A and B–B is parallel to the slope of polarogram *a*, and gives a constant net current value at its intersection with polarograms *b* and *c*. Each line yields two values of the applied voltage, which are related to a defined current value in the lifetime of a mercury drop (*e.g.*, average, maximum or minimum current). The difference between each pair of values of applied voltage, related to a constant net current measured at the same instant in the mercury-drop cycle, is equal to the difference in potential between the two solutions used for depicting polarograms *b* and *c*, since the voltage drop is the same (ignoring variations of the residual current for each set of values of applied voltage). The measured potential differences, obtained for A–A and B–B in Fig. 1, related to average current values, are *ca.* 33 and 120 mV, respectively. This leads to the conclusion that the potential difference is a function of the current at which the measurement is made, and increases as the current approaches the value of the diffusion current in *b*. For the ratio of concentrations used, 1·5 : 1, the potential difference expected on the basis of direct potentiometry at zero current is only 10·4 mV at 25°, for a one-electron reaction. The present method of measurement seems to offer an advantage over conventional potentiometry, provided that a proper choice of the current value is made.

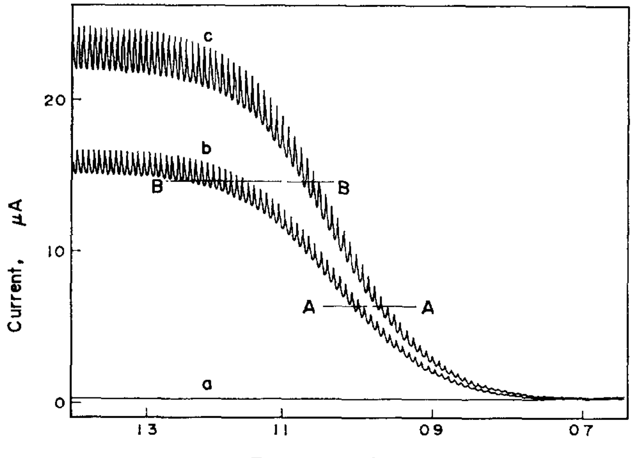


FIG. 1.—Polarograms of 0·1*M* NaOH supporting electrolyte, (a) alone; (*b*) 9·50 × $10^{-4}M$ in chromate; (*c*) 1·425 × $10^{-3}M$ in chromate. The polarograms were highly damped for illustrative purposes only.

This behaviour is unique to the d.m.e., which is a microelectrode with a periodically renewed surface at which electrolysis proceeds without stirring. Under these conditions, immediate polarization of the electrode results when the potential is set to a value corresponding to the rising part or the plateau of the current–potential curve, and is accompanied by a steady flow of current through the polarographic cell. Current reproducibility with time is achieved at a defined potential under conventional polarographic working conditions, as no measurable depletion in bulk concentration occurs during electrolysis, over a reasonable length of time, and a steady ratio of surface activities of the redox couple is established. If various concentrations of a pure compound are used, a constant current will cause various ratios of surface activities of the redox forms of the reactant to prevail, *i.e.*, various values of potential. However, potential is the independent variable whenever conventional polarography is used, suggesting that the present method of measurement is not potentiometry in the classical sense of the term, as opposed to potentiometry at a constant current applied to the d.m.e., in which case the potential is the dependent variable.[2] Other microelectrodes are usually not as suitable as the d.m.e. because they lack periodic surface renewal of the latter and therefore a steady potential is less likely to prevail when a constant current is maintained in the absence of stirring. With a macroelectrode, constant current and constant potential can under no circumstances be achieved simultaneously. Even potentiometry using the d.m.e. at constant applied current is less satisfactory than the present method, mainly on account of potential oscillations during the lifetime of the drops. This is shown by the potential–current relationships obtained with the constant-current polarographic method, developed by Ishibashi and Fujinaga.[3–5] Contrary to conventional polarographic behaviour (where only very slight oscillations in potential are obtained when the current oscillates at a given applied voltage), a constant current applied to the d.m.e. produces wide oscillations in potential which increase in magnitude as the applied current approaches the limiting current. The reason for these oscillations is the periodic variation in the surface area of the electrode. Consider the reduction of chromate ion in sodium hydroxide supporting electrolyte. Early in the drop life, when the diffusion current is small, a constant current, higher than the instantaneous diffusion current, drives the potential of the drop into the region of supporting-electrolyte discharge and simultaneous reduction of chromate and sodium ions occurs during this early stage. Then, as the drop grows, the potential returns (through a region over which the sodium will be stripped out of the drop) to more positive values, eventually reaching the rising part of the chromate reduction wave.[2]

In this paper, simple relationships between the potential change and concentration have been derived from current–potential relationships, both for reversible and irreversible electrode reactions at the d.m.e. These relationships permit the calculation of the potential difference expected for varying concentration ratios. Graphical interpretation and experimental verification of the derived equations are presented. A discussion of specific applications with a special reference to the irreversible reduction of chromate ion in alkali supporting electrolyte is also included.

THEORETICAL DISCUSSION

Reversible electrode processes

The theory of the current–potential relationship for reversible electrode processes has been the subject of discussion of numerous papers and books. The explicit treatment given by Meites,[6] for the various reversible half-reactions occurring at the d.m.e., served as a starting point for the present treatment.

If the diffusion current is proportional to concentration then the potential difference at a constant current i, maintained at the d.m.e., for two concentrations of a pure constituent involved in a reversible reaction is given by the equation

$$\Delta E_{\text{d.e.}} = (E_{\text{d.e.}})_2 - (E_{\text{d.e.}})_1 = \frac{RT}{nF} \ln \frac{i_{\text{d},2} - i}{i_{\text{d},1} - i} \tag{1}$$

The terms appearing in equation (1) have their usual meaning[6] and the numerical subscripts correspond to the solutions used for measurements. The potential refers to the average current value in the lifetime of a drop, for reversible reactions. Equation (1) applies to a variety of diffusion-controlled cases, such as the reduction of a simple metal ion, complexed metal ion, or cationic groups (*e.g.* NH_4^+ and RNH_3^+) forming the corresponding amalgams and also reductions involving only species in solution. In the case of the reversible oxidation of dropping mercury amalgams to form a simple metal ion, a complexed metal ion or a cationic group, and for oxidations involving only species in solution, equation (1) applies in essence, except that the anodic currents, denoted by subscript a, have the opposite sign. The equation for anodic reactions is

$$\Delta E_{\text{d.e.}} = (E_{\text{d.e.}})_2 - (E_{\text{d.e.}})_1 = \frac{RT}{nF} \ln \frac{(i_{\text{d}})_{\text{a},1} - i_{\text{a}}}{(i_{\text{d}})_{\text{a},2} - i_{\text{a}}} \tag{2}$$

For composite cathodic–anodic waves, each section can be treated independently, using either of the equations above. The only exception is the rare case of reversible processes involving a solid that is insoluble in mercury and formed by the reduction of metal ion. In this case the potential difference is given by:

$$\Delta E_{\text{d.e.}} = \frac{RT}{nF} \ln \frac{i_{\text{d},1}(i_{\text{d},2} - i)}{i_{\text{d},2}(i_{\text{d},1} - i)} \tag{3}$$

It is convenient to substitute new parameters x and y into equations 1, 2 and 3. When $i_{d,2} \geqslant i_{d,1}$, or $(i_d)_{a,2} \geqslant (i_d)_{a,1}$, then

$$y = \frac{i_{d,2}}{i_{d,1}} \text{ (cathodic)}$$

and

$$y = \frac{(i_d)_{a,2}}{(i_d)_{a,1}} \text{ (anodic)}$$

(y also corresponds to the ratio of concentrations of the solutions). The parameter x is defined as the ratio of the current at which the measurement of potential is made to the diffusion current of the solution of lower concentration, *i.e.*,

$$x = \frac{i}{i_{d,1}} \quad \text{(cathodic)}$$

or

$$x = \frac{i_a}{(i_d)_{a,1}} \quad \text{(anodic)}$$

Thus equation (1) can be rewritten for cathodic waves, as

$$\Delta E_{d.e.} = \frac{RT}{nF} \ln \frac{y - x}{1 - x} \tag{4}$$

and for anodic waves equation (2) may be rewritten as

$$\Delta E_{d.e.} = \frac{RT}{nF} \ln \frac{1 - x}{y - x} \tag{5}$$

and equation (3) becomes

$$\Delta E_{d.e.} = \frac{RT}{nF} \ln \frac{y - x}{y(1 - x)} \tag{6}$$

The present treatment will be limited to the case of cathodic waves described by equation (4) as, in essence, the same conclusions apply to anodic waves in equation (5), and the case of equation (6) is rare. At 25° and when the potential difference is expressed in mV, equation (4) may be rewritten as

$$\Delta E_{d.e.} = \frac{59{\cdot}15}{n} \log \frac{y - x}{1 - x} \tag{7}$$

It is seen from (7) that a plot of various measured values of $\Delta E_{d.e.}$ *vs.* $\log (y - x)/(1 - x)$, is a straight line with a positive slope of $59{\cdot}15/n$ mV and an intercept of zero. The same result is obtained with constant x and variable y as with variable x and constant y. Although such plots do not provide a simplification over the conventional technique of obtaining the same information from a single polarogram, they still offer a new alternative. Furthermore, as $x \rightarrow 0$, equation (7) reduces to

$$\Delta E_{d.e.} \sim \frac{59{\cdot}15}{n} \log y \tag{8}$$

In this limiting case, the equation approaches the form of the equation describing similar measurements with conventional potentiometry at zero current, provided the activity coefficient of the measured solutions remains constant, viz.

$$\Delta E = \frac{59 \cdot 15}{n} \log \frac{c_2}{c_1} \tag{9}$$

However, as $x \to 1$, for a constant y unusual amplification of the potential change with concentration results, depending on the value of x. A graphical interpretation of this concept is given in the family of curves of Fig. 2, in which $\Delta E_{\text{d.e.}}$ for a one-electron reduction is plotted *vs* x, for various values of y, taken to be constant in each case, on the basis of equation (7). From equation (9), the expected potential increment by conventional potentiometric methods for a one-electron reaction for *e.g.*, $y = 2$, may be calculated to be 17·8 mV. The potential differences by the present method of measurement are expected to be 61·6 mV for $x = 0{\cdot}90$ and 102 mV for $x = 0{\cdot}98$. Another interesting graphical interpretation of equation (7) is given in Fig. 3 where $\Delta E_{\text{d.e.}}$ is plotted *vs* y, for a constant value of x in each case. A family of curves is obtained for various values of x, indicating the advantages of the choice of conditions under which y is small for any constant value of x. From equation (9), for a one-electron reaction a change of 1 % in concentration (or $y = 1{\cdot}01$), causes an expected potential change of 0·26 mV, and from equation (7), under the same conditions, changes of 2·5 and 10·4 mV are expected for $x = 0{\cdot}90$ and 0·98 respectively.

Irreversible electrode processes

Meites and Israel[7] developed an equation describing the current–potential relationship at the d.m.e. for a totally irreversible process, the rate of which is governed by a single transfer step. The equation was derived from relationships that were previously presented for such an electrode reaction by Koutecký.[8] Smith, McCord

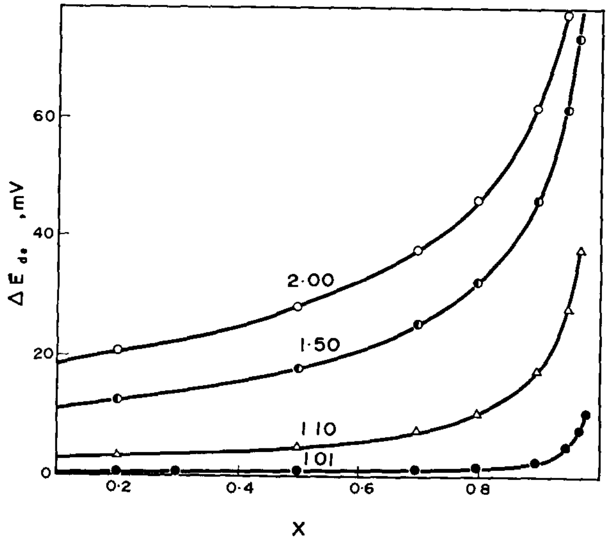


FIG. 2.—Plots of $\Delta E_{\text{d.e.}}$ *vs.* x for a given y; each curve represents equation (7), when $y = 1{\cdot}01$, $1{\cdot}10$, $1{\cdot}50$ and $2{\cdot}00$, respectively.

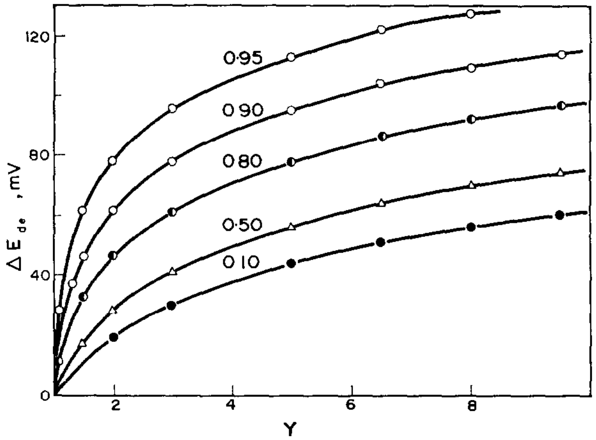


FIG. 3.—Plots of $\Delta E_{d.e.}$ *vs.* y for a given value of x; each curve represents equation (7), when $x = 0{\cdot}10$, $0{\cdot}50$, $0{\cdot}80$, $0{\cdot}90$ and $0{\cdot}95$, respectively.

and Hung[9] examined Meites and Israel's equation and found its accuracy to be sufficient to permit its use in most mechanistic and kinetic applications. This equation[7] can be expressed, in mV and for 25°, as follows:

$$E_{\mathrm{d.e.}} = \frac{59{\cdot}15}{\alpha n}\log\frac{1{\cdot}349k^{0}_{\mathrm{f,h}}}{D} - \frac{54{\cdot}2}{\alpha n}\left(\log\frac{i}{i_{\mathrm{d}}-i} - 0{\cdot}546\log t\right) \tag{10}$$

where D is the diffusion coefficient of the oxidant, α is the transfer coefficient, $k^{0}_{\mathrm{f,h}}$ is the potential-independent rate constant of the forward heterogeneous electrode reaction,[10] and i and i_{d} refer to maximum currents in the lifetime of a mercury drop. Equation (10) is conveniently separated into two terms; the second is dependent on potential and the first is not. This accounts for including the lifetime of the mercury drop, t, in the second term.[6]

From equation (10) and a similar treatment to that applied above for the case of reversible reactions, the potential difference (in mV and for 25°) at constant current at the d.m.e. used for a totally irreversible reduction, is described by the following equation:

$$\Delta E_{\mathrm{d.e.}} = \frac{54{\cdot}2}{\alpha n}\left(\log\frac{i_{\mathrm{d,2}}-i}{i_{\mathrm{d,1}}-i} + 0{\cdot}546\log\frac{t_2}{t_1}\right) \tag{11}$$

With the same definitions of y and x as before but noting that i and i_{d} refer now to the maximum current in the lifetime of the mercury drop, equation (11) becomes:

$$\Delta E_{\mathrm{d.e.}} = \frac{54{\cdot}2}{\alpha n}\left(\log\frac{y-x}{1-x} + 0{\cdot}546\log\frac{t_2}{t_1}\right) \tag{12}$$

Interpretation of equation (12) is analogous to that of equation (7) and suggests that a linear relationship intercepting the origin is expected, with a positive slope of $54{\cdot}2/\alpha n$ (in mV at 25°) when a plot of the measured values of $\Delta E_{\mathrm{d.e.}}$, for various values of x, is made at a constant y *vs.* $[\log(y-x)/(1-x) + 0{\cdot}546\log(t_2/t_1)]$. The same results are obtained for the relationship above, if the plot is made with variable y and constant x. Both plots provide an alternative method for the calculation of the transfer coefficient of the forward reaction. Furthermore, a family of curves is obtained, both when the plot is made for various values of x with constant y and *vice versa*. The general shape of all curves correspond to the curves in Figs. 2 and 3 for reversible reactions, except for the larger potential differences, obtained under identical conditions, in the case of a totally irreversible reaction. The differences are also dependent on the value of α, which is always less than 1. For $\alpha n = 0{\cdot}35$, a value reported for the reduction of chromate ion in $0{\cdot}1M$ sodium hydroxide supporting electrolyte,[7] and for $y = 2$, the expected potential differences are 161·3 and 264·5 mV for $x = 0{\cdot}90$ and 0·98 respectively. For the same transfer coefficient, the expected potential differences for $y = 1{\cdot}01$ and for $x = 0{\cdot}90$ and 0·98, are 6·4 and 27·3 mV respectively. It seems that the present method of measurement is especially advantageous when applied to totally irreversible electrode reactions.

EXPERIMENTAL

Analytical-grade reagents were used for the preparation of the standard solutions and the supporting electrolytes. Argon, after washing with a solution of chromium(II) in dilute sulphuric acid kept over amalgamated zinc, was used for the deaeration of the tested solutions. Mercury was cleaned by passing it through a pin-hole in a filter paper bubbling air through it for a few days after covering it with 8% nitric acid, then washing, degreasing, pin-hole filtering, drying[11] and double-distilling.

Polarograms were obtained with a Metrohm recording instrument, Polarecord E 261 R, after internal calibration of the potential and the current, but often the initial and span voltages were measured at the time of experiment with a Honeywell potentiometer model 2730. In some instances, the measurements of applied voltage were made by using Metrohm E 446 iR compensator. Experimental validity of equations (7) and (12) were usually verified by measurements of $E_{d.e.}$ and $\Delta E_{d.e.}$ from polarograms recorded at the slowest scan speed of *ca.* 1·4 mV/sec for the reversible reduction of thallous ion in $0{\cdot}1M$ potassium chloride supporting electrolyte and at a faster scan speed of *ca.* 2·8 mV/sec. for the irreversible reduction of chromate ion in 0·1 M sodium hydroxide supporting electrolyte. However, in the more detailed and accurate measurements made for the chromate system, either the recording 'polarograph or the manual polarograph previously described[12] was used both as a polarizing unit and as an indicator to maintain a constant maximum current, throughout a set of measurements. The minimum values of potential (which corresponded to maximum current values), were measured, under these conditions, with a Sargent model DR expanded-scale pH meter provided with mechanical digital readout corresponding to 0·2 mV/division. The polarographic cell used was supplied by Radiometer, and had a separate saturated calomel reference electrode, which was connected to the main cell compartment by an easily removable agar agar–saturated potassium chloride bridge, which was often replaced after prolonged use with alkaline solutions. The cell was immersed in a thermostat maintained at 25 ± 0·1°.

1. RESULTS AND CONCLUSIONS

Recorded polarograms for two concentrations of standard solution, corresponding to a defined value of y, were used for the measurement of $\Delta E_{d.e.}$ as a function x, adopting the approach used for Fig. 1.

The reduction of thallous ion in $0{\cdot}1M$ potassium chloride supporting electrolyte, containing 0·002% Triton X-100 as a maximum suppressor, was studied as a representative example of the reversible electrode reactions described by equation (7). For $y = 1{\cdot}36$ ($6{\cdot}43 \times 10^{-4}$ and $4{\cdot}73 \times 10^{-4}M$ solutions), and $x = 0{\cdot}12$–$0{\cdot}94$, the measured values of $\Delta E_{d.e.}$ gave a linear relationship with a positive slope of 59·6 mV when plotted against $\log (y - x)/(1 - x)$, with an intercept of less than 1 mV on the ΔE axis. Each of measured values of $\Delta E_{d.e.}$, for x ranging from 0·34 to 0·94, was used to calculate y, by applying equation (7) in the form

$$y = \left(\operatorname{antilog} \frac{\Delta E_{d.e.}}{59{\cdot}15}\right)(1 - x) + x \qquad (7a)$$

yielding values of y within $\pm 3\%$ of the ratio of concentrations used. Other ranges of concentrations of thallous ion were also tested, for values of y from 1·20 to 2·26, yielding a straight line passing through the origin in each case, and with slopes in the range 57–60 mV.

The validity of equation (12), describing totally irreversible reactions, was tested by using the reduction wave of chromate ion in 0·1M sodium hydroxide supporting electrolyte. For $y = 1{\cdot}50$ ($1{\cdot}425 \times 10^{-3}$ and $9{\cdot}50 \times 10^{-4}M$ solutions), and $x = 0{\cdot}12$–$0{\cdot}95$, the values of $\Delta E_{\mathrm{d.e.}}$, were plotted *vs.* $[\log (y - x)/(1 - x) + 0{\cdot}546 \log (t_2/t_1)]$ and gave a linear relationship with a positive slope of 147 mV (Fig. 4) corresponding to $\alpha n = 0{\cdot}37$, as compared with a value of 0·35 obtained previously by extremely careful experiment.[7] However, the intercept obtained by extrapolating curve *a* of Fig. 1 yielded a value of 12 mV for $\Delta E_{\mathrm{d.e.}}$. This discrepancy from the expected behaviour which is described by the dashed line *b* in Fig. 4 (calculated for $\alpha n = 0{\cdot}35$), was reproducible, and the calculation of y from the measured values of $\Delta E_{\mathrm{d.e.}}$, for a totally irreversible reaction, requires the introduction of experimentally determined values of the slope, s, and the intercept, a, into equation (12) as follows:

$$\Delta E_{\mathrm{d.e.}} = a + s\left[\log\frac{(y-x)}{(1-x)} + 0{\cdot}546 \log\frac{t_2}{t_1}\right] \tag{12a}$$

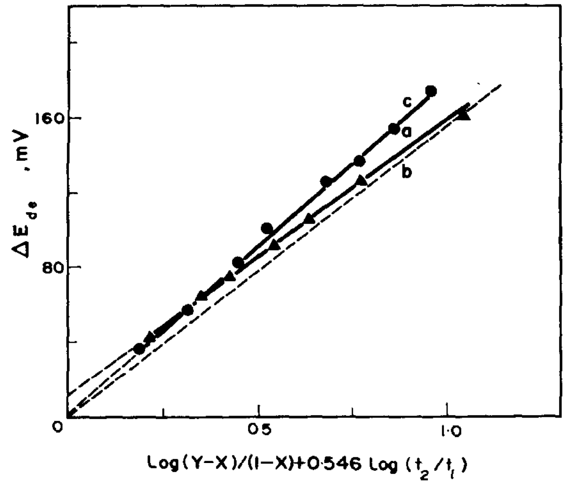


FIG. 4.—Log plots, corrected for variations of charging current, for the polarograms of $9{\cdot}50 \times 10^{-4}M$ and $1{\cdot}425 \times 10^{-3}M$ chromate in 0·10M sodium hydroxide: (*a*) no gelatin; (*b*) a theoretical plot representing equation (12) for $\alpha n = 0{\cdot}35$; (*c*) containing 0·005% gelatin.

The occurrence of the intercept, *a*, was puzzling, and it was suspected that a minor maximum might be responsible for the distortion of the current–potential relationship, especially since a maximum was developed if the polarographic system was left to stand. Evidence for this postulate is given by curve *c* in Fig. 4. Conditions identical to those for curve *a* in Fig. 4a, were used except that the ratio y was 2 and the solutions contained 0·005% gelatin as a maximum suppressor. A straight line passing through the origin was obtained, and had a slope of 185 mV, corresponding to $\alpha n = 0{\cdot}293$. Maximum suppressors and other surface-active agents are known to influence kinetic parameters in this fashion, usually decreasing the value of αn.[13] A more detailed study, with various concentrations of gelatin, was not performed in the present work, though such a study should provide information concerning the variation of αn with gelatin concentration, and the minimum concentration of gelatin required to obviate the maximum without affecting αn.

When an external expanded-scale potentiometer was used to measure $E_{\text{d.e.}}$ for various concentrations of chromate in $0{\cdot}1M$ sodium hydroxide supporting electrolyte, after adjustment of the applied voltage to maintain a constant current, the potential oscillated during the drop lifetime, yielding minimum potential at the maximum current and *vice versa*. The potential gradient (between minimum and maximum values of potential) is reported in Table I, which shows some of the experiments performed for various concentrations and currents, in the absence or presence of 0·005% gelatin as a maximum suppressor. From the results in Table I, it is seen that the potential gradient is due not only to the iR-drop variation resulting from current oscillations, but also to a potential gradient which diminishes upon the addition of a maximum suppressor (*cf.* the results obtained for $1{\cdot}90 \times 10^{-3}M$ chromate solutions, in columns 2 and 4). The latter potential gradient is not only dependent on the current magnitude but also on the ratio of i/i_d for each concentration (*cf.* columns 2 and 3), and is most likely linked with the existence of polarographic maxima. A detailed discussion of the implications of the difference in potential gradient in the presence and absence of gelatin is beyond the present paper. However, surface coverage of the mercury drop by the adsorption of maxima suppressors, has been reported by various authors to lower the surface tension and flatten the electrocapillary curves over a wide range of potential. The present study serves not only as an alternative for obtaining n or αn values but also serves as a new tool for the elucidation of fundamental problems.

TABLE I.—THE INFLUENCE OF A MAXIMUM SUPPRESSOR ON THE POTENTIAL GRADIENT* IN THE LIFETIME OF MERCURY DROPS

$i_{\max}$, μA	Potential gradient, mV*			
	—		0·005% gelatin	
	$1{\cdot}90 \times 10^{-3}M$	$1{\cdot}90 \times 10^{-4}M$	$1{\cdot}90 \times 10^{-3}M$	$1{\cdot}14 \times 10^{-3}M$
17·4	4·0		1·1	1·0
15·4	3·0		0·9	0·8
13·4	—		0·8	0·7
10·4	1·8		0·6	0·6
7·4	1·2		0·5	0·4
2·1	0·2	3·6	0·1	0·1
1·9	—	3·4	—	—

Measured for potassium chromate in $0{\cdot}1M$ NaOH, using an external expanded-scale potentiometer for various constant current values.

* See text.

To examine the dependence of $\Delta E_{\text{d.e.}}$ on y at a constant value of x, the minimum values of $E_{\text{d.e.}}$ were measured with an expanded-scale potentiometer for 0·95–2·5 mM chromate in $0{\cdot}1M$ sodium hydroxide containing 0·005% gelatin. Plots of $\Delta E_{\text{d.e.}}$ *vs.* $[\log (y - x)/(1 - x) + 0{\cdot}546 \log (t_2/t_1)]$ for each constant value of x were linear, and passed through the origin within experimental error. The calculated αn values for x varying from 0·12 to 0·90 varied from 0·286 to 0·300. These results show that application of the method described should prove useful for analytical purposes within limited concentration ranges.

A specific analytical application of the present method is accurate determination, especially when irreversible reactions with low αn values are involved. To give high accuracy, the method should display a detectable potential change for a slight change in concentration. This criterion was fulfilled for chromate ion in 0·1M sodium hydroxide, in the absence of gelatin, when the measurements were made at a high value of x, namely 0·9542. The results are given in Table II, y being calculated from $(\Delta E_{\text{d.e.}})_{\text{min}}$, according to the following equation, when variations in t are justifiably ignored:

$$y = \left[\text{antilog} \frac{(\Delta E_{\text{d.e.}})_{\text{min}}}{s}\right](1 - x) + x \qquad (12b)$$

where s equals 147 mV, the slope found in the absence of gelatin. The deviations calculated in Table II are very low, indicating the suitability of the method for accurate determinations. Determinations can be made after prior estimation of the concentration, by measuring the $\Delta E_{\text{d.e.}}$ of the solution against a standard solution having similar concentration. Although such an approach is not analogous to differential spectrophotometry, it strongly resembles it.

TABLE II.—DETERMINATION OF CHROMATE ION FROM POTENTIAL DIFFERENCES DUE TO LOW CONCENTRATION CHANGE

y, taken	$\Delta E_{\text{min}}, mV$	y, calc.*	Error, %
1·0020	3·6	1·0027	0·07
1·0040	6·0	1·0045	0·05
1·0070	9·5	1·0074	0·04
1·0100	14·0	1·0112	0·12

Measurements of minimum potential readings, $(E_{\text{d.e.}})_{\text{min}}$, were made for $x = 0{\cdot}9542$, using an expanded-scale potentiometer. ΔE_{min} is the difference in potential when the measured solutions were compared with a $9{\cdot}5 \times 10^{-4}$ solution of chromate in 0·1M NaOH.

* See text.

Davis and Shalgosky[14] and Davis and Seaborn[15] proposed the use of a differential cathode-ray polarograph with twin electrodes for accurate and precise determinations, using the method of comparative polarography. In the latter, a differential curve was recorded by using two cells, one containing the solution to be analysed and the other a similar solution of accurately known composition. Using twin electrodes and twin cells for direct measurement of $\Delta E_{\text{d.e.}}$ resembles the ideas involved in comparative polarography, and should prove advantageous for precise determinations.

The results of the present work agree well with equations (7) and (12), verifying the postulates in the theoretical discussion and demonstrating the use of this new method in fundamental studies as well as for analytical applications.

Acknowledgement—The permission of the management of IMI, Institute for Research and Development, to publish this work is gratefully acknowledged. My thanks are due to Miss Z. Shapira for performing part of the experimental work and I am indebted also to Professor Louis Meites, Chairman of the Department of Chemistry, Clarkson Institute of Technology, Potsdam, New York, for his helpful comments and discussions.

Zusammenfassung—Bei einem neuen Analysenverfahren wird das Potential einer Quicksilbertropfelektrode in Abhängigkeit von der Konzentration eines elektroaktiven Lösungsbestandteils gemessen, wobei durch Regelung der an die polarographische Zelle angelegten Spannung ein konstanter Strom aufrechterhalten wird. Es werden Gleichungen abgeleitet, die die Potentialänderung bei Änderung der Konzentration eines Bestandteils voraussagen, der an einer reversiblen oder irreversiblen Elektrodenreaktion teilnimmt. Die abgeleitete Gleichung wird graphisch interpretiert; dabei zeigen sich die besten Versuchsbedingungen für die Potentialmessungen. Es ergeben sich viel größere Potentialdifferenzen als bei der herkömmlichen Potentiometrie, insbesondere, wenn das Verfahren auf irreversible Elektrodenreaktionen an der Quecksilbertropfelektrode angewandt wird. Es werden Versuchsergebnisse mitgeteilt, die nicht nur alle Erwartungen erfüllen, sondern auch zeigen, daß das Verfahren einen neuen Weg zur Erforschung einiger grundlegender Probleme weist.

Résumé—On décrit une nouvelle méthode dans laquelle le potentiel de l'électrode à goutte de mercure tombante est mesuré en fonction de la concentration d'un constituant électroactif lorsqu'on maintient un courant constant en adjustant le voltage appliqué à la cellule polarographique. On en déduit des équations décrivant le changement de potentiel attendu causé en faisant varier la concentration d'un constituant impliqué dans une réaction d'électrode réversible ou irréversible. On effectue des interprétations graphiques de l'équation dérivée, indiquant les conditions les plus convenables pour effectuer les mesures de potentiel, donnant des différences de potentiel qui excèdent fortement celles obtenues par la potentiométrie classique, particulièrement lorsque la méthode est appliquée à des réactions d'électrode irréversibles à l'électrode à goutte de mercure tombante. On présente des arguments expérimentaux qui non seulement vérifient toutes les prévisions, mais qui indiquent aussi que la méthode offre un nouvel accès à l'étude de quelques problèmes fondamentaux.

REFERENCES

1. Y. Israel, *Anal. Chem.*, 1959, **31**, 1473.
2. L. Meites, private communications.
3. M. Ishibashi and T. Fujinaga, *Denki Kagaku*, 1956, **24**, 375; 525.
4. *Idem*, *Anal. Chim. Acta*, **18**, 112.
5. T. Fujinaga, in *Progress in Polarography*, P. Zuman and I. M. Kolthoff, eds., Vol. 1, pp. 201–221. Interscience, New York, 1962.
6. L. Meites, *Polarographic Techniques*, 2nd Ed., pp. 203–266. Interscience, New York, 1965.
7. L. Meites and Y. Israel, *J. Am Chem. Soc.*, 1961, **83**, 4903.
8. J. Koutecký, *Collection Czech. Chem. Commun.*, 1953, **18**, 597.
9. D. E. Smith, T. G. McCord and H. L. Hung, *Anal. Chem.*, 1967, **39**, 1149.
10. P. Delahay, *New Instrumental Methods in Electrochemistry*, pp. 32–36. Interscience, New York, 1954.
11. Y. Israel, *Analyst*, 1958, **83** 432.
12. Y. Israel and A. Vromen, *Anal. Chem.*, 1959, **31**, 1470.
13. A. N. Frumkin, *Dokl. Akad. Nauk* S.S.S.R, 1952, **85**, 373.
14. H. M. Davies and H. I. Shalgosky, in *Advances in Polarography*, I. S. Langmuir, ed., Vol. 2, pp. 618–27.
15. H. M. Davies and J. E. Seaborn, in *Advances in Polarography*, I. S. Langmuir, ed., Vol. 1, pp. 239–50.

Talanta, 1972, Vol. 19, pp. 1079 to 1081. Pergamon Press. Printed in Northern Ireland

NOTE

Nomenclature in thermal analysis—II

The recommendations in the First Report of the Nomenclature Committee of the International Confederation for Thermal Analysis (ICTA)[1] have been generally well received and are at present being considered for adoption by both the International Union of Pure and Applied Chemistry and the International Standards Organization. Considerable interest has also been shown by individual scientists.[2]

Since these proposals were promulgated, the Committee have drawn up a further report, the recommendations in which have been endorsed in Business Session at the Third International Conference on Thermal Analysis at Davos, Switzerland, in August, 1971. The Council of ICTA have therefore directed that this Second Report be also published as a definitive document of ICTA, with the recommendation that the conventions set out therein be adhered to in all publications in the English language. Background information on the reasons for adoption of certain conventions has already been published.[3]

The Sub-Committees dealing with the German, Japanese and Russian languages[1] have all been active and a nomenclature system in Japanese, based on the recommendations in the First Report, has now been published.[4]

I. AMPLIFICATION OF FIRST REPORT

Because of the variety of opinions expressed on, and the different interpretations of, the term *pyrolysis*, the Committee consider the time inopportune to promulgate on *thermal decomposition* and related terms—see First Report, Section I(*f*).

Some confusion appears to have arisen over the term *isobaric weight-change determination* as defined in the First Report, Section IIIB, Sub-section 1. The Committee consider that this confusion could be obviated by the following statement.

> In the context of the report published in *Talanta*, 1969, **16**, 1227, Section IIIB, Sub-sections 1 and 2 headed, respectively, *Static* and *Dynamic*, these terms refer to environmental temperature. It should be noted that the same terms are also used with reference to environmental atmosphere.

II. DTA AND TG APPARATUS AND TECHNIQUE

In considering the terms available, certain arbitrary choices have had to be made—*e.g.*, between *specimen* and *sample*—but the only term in fairly common use that is rejected is *inert material.*

A. DTA

The *sample* is the actual material investigated, whether diluted or undiluted.

The *reference material* is a known substance, usually inactive thermally over the temperature range of interest.

The *specimens* are the sample and reference material.

The *sample holder* is the container or support for the sample.

The *reference holder* is the container or support for the reference material.

The *specimen-holder assembly* is the complete assembly in which the specimens are housed. Where the heating or cooling source is incorporated in one unit with the containers or supports for the sample and reference material, this would be regarded as part of the specimen-holder assembly.

A *block* is a type of specimen-holder assembly in which a relatively large mass of material is in intimate contact with the specimens or specimen holders.

The *differential thermocouple** or ΔT *thermocouple** is the thermocouple* system used to measure temperature difference.

B. TG

A *thermobalance* is an apparatus for weighing a sample continuously while it is being heated or cooled.

* Should another thermosensing device be used, its name should replace *thermocouple* in these terms.

The *sample* is the actual material investigated, whether diluted or undiluted.†

The *sample holder* is the container or support for the sample.

C. DTA and TG

The *temperature thermocouple** or *T thermocouple** is the thermocouple* system used to measure temperature: its position with respect to the sample should always be stated.

The *heating rate* is the rate of temperature increase, which is customarily quoted in degrees per minute (on the Celsius or Kelvin scales). Correspondingly, the cooling rate is the rate of temperature decrease. The heating or cooling rate is said to be *constant* when the temperature/time curve is linear.

In simultaneous DTA–TG, definitions follow from those given for DTA and TG separately.

III. DTA AND TG CURVES

The Committee, in reaffirming their decision to use the terms *differential thermal curve* or *DTA curve*, *thermogravimetric curve* or *TG curve* and *derivative thermogravimetric curve* or *DTG curve*, recommend disuse of the other terms which have appeared in the literature, such as thermogravimetric analysis curve, thermolysis curve, thermoweighing curve, thermogravigram, thermoponderogram, thermogram, differential thermogravimetric curve, differential thermogram, derivative thermogram, polytherm, *etc.*

Certain conventions and reporting procedures for DTA and TG curves have already been specified in *Anal. Chem.*, 1967, **39**, 543, and in the First Report. The following definitions are to be read in conjunction with these recommendations.

A. DTA

In DTA **it must be remembered** that although the ordinate is conventionally labelled ΔT the output from the ΔT thermocouple will in most instances vary with temperature and the measurement recorded is normally the e.m.f. output, E, *i.e.*, the conversion factor, b, in the equation $\Delta T = bE$ is not constant since $b = f(T)$, and that a similar situation occurs with other sensor systems.

All definitions refer to a single peak such as that shown in Fig. 1: multiple peak systems, showing shoulders or more than one maximum or minimum, can be considered to result from superposition of single peaks.

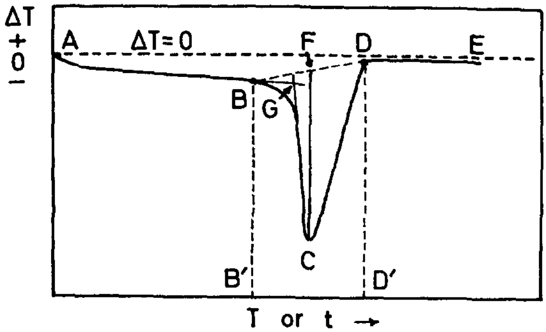


Fig. 1.—Formalized DTA curve.

The *base line* (AB and DE, Fig. 1) corresponds to the portion or portions of the DTA curve for which ΔT is approximately zero.

A *peak* (BCD, Fig. 1) is that portion of the DTA curve which departs from and subsequently returns to the base line.

An *endothermic peak* or *endotherm* is a peak where the temperature of the sample falls below that of the reference material; that is, ΔT is negative.

An exothermic peak or *exotherm* is a peak where the temperature of the sample rises above that of the reference material; that is, ΔT is positive.

---

* Should another thermosensing device be used, its name should replace *thermocouple* in these terms.

† Samples used in TG are normally not diluted, but in simultaneous TG and DTA diluted samples might well be used.

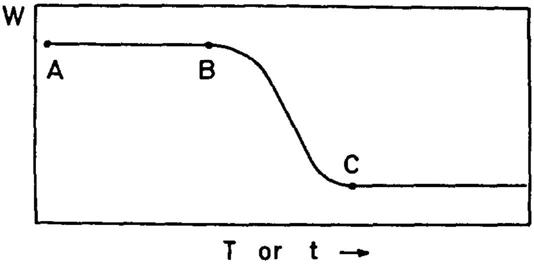


FIG. 2.—Formalized TG curve.

Peak width (B′D′, Fig. 1) is the time or temperature interval between the points of departure from and return to the base line.*

Peak height (CF, Fig. 1) is the distance, vertical to the time or temperature axis, between the interpolated base line* and the peak tip (C, Fig. 1).

Peak area (BCDB, Fig. 1) is the area enclosed between the peak and the interpolated base line.*

The *extrapolated onset* (G, Fig. 1) is the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak (BC, Fig. 1) with the extrapolated base line (BG, Fig. 1).

B. TG

All definitions refer to a single-stage process such as that shown in Fig. 2: multistage processes can be considered as resulting from a series of single-stage processes.

A *plateau* (AB, Fig. 2) is that part of the TG curve where the weight is essentially constant.

The *initial temperature*, T_i, (B, Fig. 2) is that temperature (on the Celsius or Kelvin scales) at which the cumulative weight change reaches a magnitude that the thermobalance can detect.

The *final temperature*, T_f, (C, Fig. 2) is that temperature (on the Celsius or Kelvin scales) at which the cumulative weight change reaches a maximum.

The *reaction interval* is the temperature difference between T_f and T_i as defined above.

Acknowledgements—The Committee express their thanks to the Society for Analytical Chemistry for providing accommodation for meetings and secretarial facilities, to the Thermal Analysis Group of that Society for assistance rendered and to thermal analysts in many countries for cooperation in providing comments at various stages of the programme.

c/o Industrial and Laboratory Services
P.O. Box 9, Lyme Regis
Dorset, U.K.†

R. C. MACKENZIE (Chairman)
C. J. KEATTCH (Secretary)
D. DOLLIMORE
J. A. FORRESTER
A. A. HODGSON
J. P. REDFERN

REFERENCES

1. *Talanta*, 1969, **16**, 1227.
2. *Chem. Ind.*, 1970, 272, 449, 515, 643; 1971, 57.
3. R. C. Mackenzie, *J. Therm. Anal.*, in the press.
4. *Calorim. Therm. Anal. Newsletter*, 1971, 2, 45.

---

* There are several ways of interpolating the base line and that given in Fig. 1 is only an example. Location of points B and D (Fig. 1) depends on the method of interpolation of the base line.

† The address given is that of the Secretary.

Talanta, 1972, Vol. 19, p. 1083. Pergamon Press. Printed in Northern Ireland

LETTER TO THE EDITOR

Ammonium hexanitratocerate(IV) as an oxidizing agent—VII* Determination of some carboxylic acids

SIR,

Cerium(IV) sulphate has been widely used for determination of organic substances, especially acids.[1–9] The procedures generally involve heating the compound with excess of cerium(IV), cooling and back-titrating. The stoichiometry does not usually correspond to a definite oxidation path but but is fairly constant under carefully prescribed conditions. Formic acid is often an end-product, and resists further oxidation.

The earlier workers[1–8] used ceric sulphate in sulphuric acid, but Smith and Duke used the more powerful perchlorate oxidant.[9] We have found that ammonium hexanitratocerate(IV) in nitric acid medium has a reactivity between that of the sulphato and perchlorato reagents and that it gives a fixed stoichiometry for the oxidation of an organic acid over a wide range of temperature and time. The rate decreases with increasing nitrate and/or nitric acid concentration, and increases with temperature. The stoichiometry is highly favourable, ranging from 6 to 14 moles of cerium(IV) per mole of acid. Formic acid is not attacked and is usually an end-product. Results for malic, tartaric, citric and malonic acids were correct to within 1%. The main drawback is that the method cannot be applied to mixtures of acids, or to determination of the acids in the presence of other species oxidized by cerium(IV). As the method involves treatment with excess of oxidant, species such as chloride *etc* must be absent.

The procedure is as follows. $0\cdot1M$ solution of the reagent in $1M$ nitric acid is prepared and standardized with oxalate.[10] A known weight of sample is added to an excess of the oxidant, 5 ml of $10M$ nitric acid are added, and the whole is diluted to 100 ml and heated at 60° for 30 min. It is cooled, dilute sulphuric acid ($5N$ 20 ml) is added, and the excess of cerium(IV) is back-titrated with iron(II) solution in sulphuric acid, with ferroin as indicator.

The stoichiometry is 6 moles of cerium(IV) per mole of tartaric or malonic acid, 14 for citric acid, and 8 for malic acid, the products being formic acid and carbon dioxide.

Gatto and Stone[11] had previously used ammonium hexanitratocerate(IV) in acetic acid medium for oxidation of organic acids dissolved in glacial acetic acid and concluded that α-keto-acids and α-hydroxy-acids with an α-phenyl group are rapidly oxidized at room temperature and be determined accurately, that polycarboxylic hydroxy-acids are rapidly oxidized but not determinable, and that aliphatic α-hydroxy-acids are slowly oxidized and not determinable. No such difficulties seem to occur with the nitric acid system used by us.

G. GOPALA RAO
I. SUBRAHMANYAM
B. MADHAVA RAO

Department of Chemistry
Andhra University
Waltair, India

28 *October* 1971

REFERENCES

1. N. Benrath and K. Ruland, *Z. Anorg. Allgem. Chem.*, 1920, **114**, 267.
2. N. H. Furman, *J. Am. Chem. Soc.*, 1928, **50**, 755.
3. H. H. Willard and P. Young, *ibid.*, 1928, **50**, 1322.
4. J. A. Atanasiu and V. Stefanescu, *Ber.* 1928, **61**, 1343.
5. A. J. Berry, *Analyst*, 1929, **54**, 461.
6. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1930, **52**, 132.
7. N. N. Sharma and R. C. Mehrotra, *Anal. Chim. Acta*, 1954, **11**, 417 and 507.
8. I. Pais, E. Schulek and M. Rozsahegyi, *Talanta*, 1963, **10**, 445.
9. G. F. Smith and F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 120.
10. G. Gopala Rao, P. V. Krishna Rao and K. S. Murty, *Talanta*, 1962, **9**, 835.
11. J. T. Gatto and K. G. Stone, *ibid.*, 1966, **13**, 597.

---

* Part VI: *Talanta*, 1972, **19**, 59.

Zusammenfassung—Der Einfluß von Brucin auf die Reduktion von Strychnin zu Hydrostrychnin wurde untersucht und ein neues Verfahren vorgeschlagen, um vor der Bestimmung von Strychnin durch Reduktion Brucin- und Strychninsulfat zu trennen.

BIBLIOGRAPHIE

1. M. Mariaud et D. Halot, *Ann. Pharm. France*, sous presse.
2. M. Sarsunova, J. Menkynova et J. Fellegi, *Pharm. Zentralhalle*, 1962, **101**, 325
3. M. Sarsunova et J. Menkynova, *Chem. Zvesti*, 1963, **17**, 556.
4. W. Poethke et W. Kinze, *Pharm. Zentralhalle*, 1965, **104**, 489.
5. G. Duliau, *J. Chromatog.*, 1965, **19**, 172.
6. J. Zarnack et S. Pfeifer, *Pharmazie*, 1963, **18**, 288.
7. V. Wukcevic-Kovacevic et Z. Bozin, *Sci. Pharm.*, 1968, **36**, 180.
8. W. Wisniewki et A. Pietura, *Acta Polon. Pharm*, 1970, **27**, 567.
9. Fr. Jaminet, *J. Pharm. Belg.* 1953, **7**, 449.
10. A. Constantinescu et T. Stan, *Farmacia (Bucharest)*, 1963, **11**, 379.
11. R. Quilichini et R. Castagnou, *Bull. Soc. Pharm. Bordeaux*, 1955, **93**, 167.
12. M. A. Ciasca Rendina et C. Galeffi, *Ann. Ist. Super. Sanita*, 1969, **5**, 209.
13. I. S. Taylor et A. Ifrim, *J. Pharm. Pharmacol.*, 1959, **11**, 191.
14. M. Scott, A. Tanb et C. Piantadon, *J. Am. Pharm. Assoc. Sci. Ed.*, 1956, **45**, 232.
15. R. Fischer et S. Charbo, *Pharm. Zentralhalle*, 1958, **97**, 101.
16. P. Tunnan et W. Hubmann, *Arch. Pharm.*, 1954, **287**, 281.
17. W. Kamp et C. Post, *Pharm. Weeklad*, 1961, **96**, 179.
18. S. L. Tompsett, *Acta Pharmacol. Toxicol.* 1960, **17**, 295.
19. T. Yoshino, A. Seno et M. Sugihara, *Kagaku To Kogyo (Osaka)*, 1962, **36**, 404.
20. T. Yoshino et M. Sugihara, *ibid.*, 1955, **29**, 257.
21. I. Bayer et S. Farkas, *Acta Chim. Acad. Sci. Hung.*, 1964, **41**, 209.
22. S. Farkas et I. Bayer, *Acta Pharm. Hung.*, 1962, **32**, 263.
23. H. M. Perry et M. L. Sheppard, *Ann. Pharm. Pharmacol.*, 1964, **Suppl. 16**, 136.
24. B. I. Shvidkii et V. P. Kramarenko, *Farmatsevt Zh. Kiev*, 1966, **21**, 20.
25. B. W. Rehn, *J. Assoc. Offic. Anal. Chem.*, 1967, **50**, 283.
26. B. I. Shvidkii, *Pharm. Zentralhalle*, 1967, **22**, 18.
27. M. Dugandzic, *Acta Pharm. Jugoslav.*, 1971, **21**, 25.
28. M. Carlassare, *Farmaco (Pavia) Ed. Prat.* 1955, **10**, 662.
29. A. Waksmundzki et E. Soczewinski, *Acta Polon. Pharm.*, 1958, **15**, 279.
30. Ch. Bedel, *Ann. Pharm. France.* 1943, **1**, 104.
31. S. Rolland-Leclerq, *J. Pharm. Belg.*, 1947, *No. 1–2*, 283.
32. M. S. El Ridi et K. Khalifa, *Proc. Pharm. Soc. Egypt.*, 1953, **35**, 31.
33. D. Banes, *J. Am. Pharm. Assoc.*, 1954, **43**, 580.

Talanta, 1972, Vol. 19, pp. 1217 to 1221. Pergamon Press. Printed in Northern Ireland

Spectrophotometric determination of dimethyl sulphoxide

(*Received* 22 *March* 1971. *Revised* 9 *February* 1972. *Accepted* 17 *February* 1972)

Working with aqueous solutions of dimethyl sulphoxide (DMSO) has imposed the need for a quick and simple method for its quantitative determination. The existing methods are based either on the ability of the sulphoxide group to be oxidized to the sulphone, or on its ability to be reduced to the sulphide. Potassium permanganate[1,2] and, recently, chloramine-T[3] are used as oxidizing agents, titanium(III) chloride[4] and tin(II) chloride[5] as reducing agents.

Reduction with iodide in glacial acetic acid followed by the titration of liberated iodine[6] is suitable but cannot be applied to dilute aqueous solutions. The method of potentiometric titration used for the determination of the sulphoxide dissolved in acetic anhydride, when the titration is performed with an acetic anhydride[7] or dioxan[8] solution of perchloric acid, cannot be applied to such solutions either.

The oxidation methods fail in the presence of reducing agents, *e.g.*, dimethyl sulphide which is often present in the sulphoxide. The reduction methods, on the other hand, cannot be used in the presence of oxidizing agents such as dimethyl sulphone.

Our attempt to avoid these difficulties was based on the property that DMSO can cause changes in the visible absorption spectra of some metal compounds (especially compounds of the transition metals) in aqueous solution. In these solutions water and sulphoxide compete for places in the co-ordination sphere of the metal ions. Fratiello *et al.*[9] have established, from proton magnetic resonance studies, that DMSO contributes to the first co-ordination shell of aluminium ions even in the presence of a large excess of water. As a result, a change should be expected in the position of the absorption spectra, which are shifted to longer wavelengths (red shift). This medium effect has long been known.[10] We also established it by studying the absorption spectra of various metals salts in solutions containing various amounts of DMSO.[11] Though the shapes of the spectra are not essentially modified by the change of the medium, the intensities of the bands are increased and red shifts observed in the presence of DMSO. As the best result (the highest increase in intensity and the smallest shift of the band) was obtained with ammonium iron(III) sulphate the spectrophotometric determination of milligram quantities of DMSO in aqueous solutions was developed with this salt as the reagent.

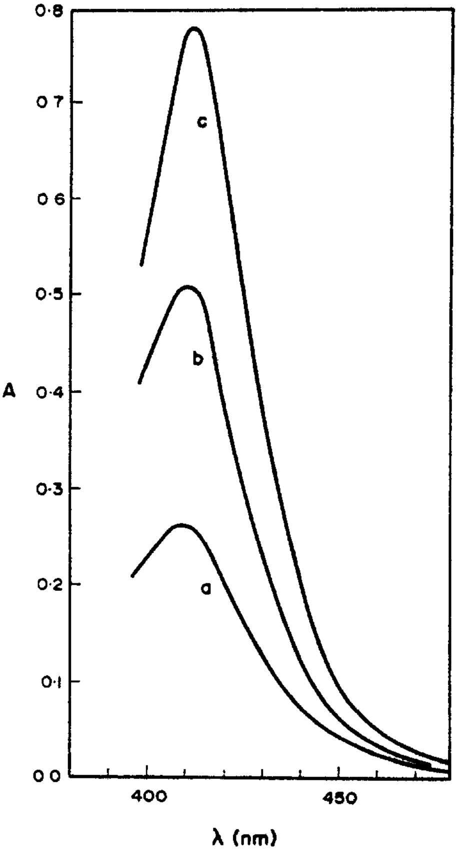


FIG. 1.—Spectra of 5·0 ml of 0·5M Fe(III) alum in 0·1M H_2SO_4, pH 1·4, diluted to 10 ml with water: (*a*) with 50·0 mg of DMSO; (*b*) with 100·0 mg of DMSO; (*c*) with 150·0 mg of DMSO, measured against the blank.

EXPERIMENTAL

Reagents

The DMSO was recrystallized three times (n_D^{20} 1·477) and stored over Linde 4A Molecular Sieve. In the visible region it showed no absorption. Other chemicals were of reagent grade quality, except for dimethyl sulphone, (Koch-Light pure grade). Doubly-distilled water was used throughout.

Procedure

The sample containing up to 200 mg of DMSO is placed in a 10-ml volumetric flask, being neutralized by addition of ammonia solution or dilute sulphuric acid if necessary, before addition of reagent. Then 5 ml of the reagent —0·5*M* iron(III) alum in 0·1*M* sulphuric acid—are added and the solution is diluted with water to the mark. After 30 min the absorbance is measured in 10-mm cells at 410 nm against a blank solution with identical concentration of the reagent. The temperature should be kept constant within ±1°. The amount of DMSO is read from the calibration curve obtained under the same conditions. Beer's law is obeyed over the DMSO concentration range up to 20 mg/ml.

RESULTS AND DISCUSSION

Spectra

The spectra are given in Fig. 1. The absorption maximum is at 410 nm, and the shift to longer wavelengths with the increase in DMSO concentration is negligible.

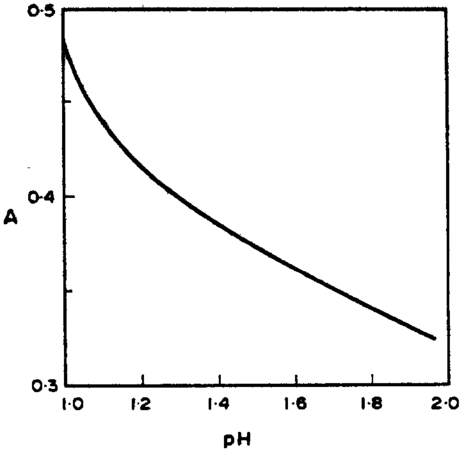


FIG. 2.—The effect of pH on the absorbance: 5 ml of 0·5*M* Fe(III) alum with 100.0 mg of DMSO, diluted to 10 ml.

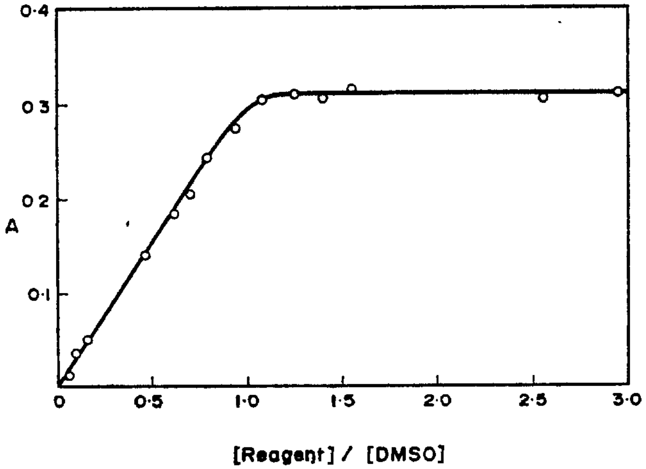


FIG. 3.—Mole-ratio plot at constant pH (1·4).

Effect of time, temperature and pH

The colour appears instantaneously on addition of the reagent, reaches full intensity in 30 min and remains stable for at least 24 hr.

With increase in temperature the absorption maximum shifts to longer wavelengths. This is due to the dependence of the nature of the solute (in the solvated form) on temperature.[12] Most frequently several solvates are involved which are in temperature-dependent mutual equilibrium.

With increase in pH, the absorbance decreases at first rapidly and then more slowly, as shown in Fig. 2. A glass electrode was used in the pH adjustment. This is quite permissible, owing to the low DMSO concentration. Kolthoff[13] showed that, under specific conditions, the glass electrode could be used even in concentrated DMSO solutions. In choosing the working value of pH 1·40, which is practically independent of the amount of DMSO, a compromise was made between sensitivity and dependence on acidity.

Effect of reagent concentration

Samples were treated as in the standard procedure except that the amount of reagent was varied to give a mole ratio of Fe(III) to DMSO ranging from 0·07 to 4. The pH was kept constant. The absorbance attained a constant value at a reagent:DMSO ratio of about 1 (Fig. 3).

Interferences

Dimethyl sulphide (pure) and dimethyl sulphone (concentrated aqueous solution) do not absorb in the visible region. In concentrations up to 25% that of the DMSO, dimethyl sulphide causes no interference. Dimethyl sulphone in amounts up to that of the DMSO content is without any effect (Table I).

TABLE I.—Effect of dimethyl sulphide (DMS) and dimethyl sulphone ($DMSO_2$) on DMSO determination.

DMSO taken, *mg*	DMS added *mg*	DMSO found, *mg*	$DMSO_2$ added *mg*	DMSO found, *mg*
100·0	0	100·0	0	100·0
100·0	5·0	100·0	5·0	100·0
100·0	25·0	100·0	25.0	100·0
100·0	50·0	103·5	50·0	100·0
100·0	75·0	106·0	75·0	100·0
100·0	100·0	110·0	100·0	100·0

Cations which interact with DMSO and especially those having spectra which are affected by DMSO, can interfere in the determination and therefore should be eliminated. This can be done by passing the sample through a small column of cation-exchanger before adding the ferric alum. We used Dowex 50-X8 [Na^+, 60-100 mesh] as the cation-exchanger. In one experiment the sample contained 200·0 mg of DMSO and 1·0 mg each of Ni, Co(II), Cr(III), U(VI) and Fe(III) sulphates in aqueous solution. The effluent as well as the water used for rinsing the column were collected in a 10-ml volumetric flask from which 5 ml were taken for the spectrophotometric determination. The experiment was repeated eight times and the mean value of 100·0 ± 1·1 mg obtained. It is evident that DMSO is quantitatively recovered from the resin, which is in agreement with an earlier finding,[8] and also proves the correctness of the method used for elimination of interfering cations.

Precision and accuracy

Solutions containing known amounts of DMSO were analysed ten times according to the recommended procedure. Averages and standard deviations were: 49·5 ± 0·5 mg (50·0 mg taken), 100·0 ± 0·5 mg (100·0 mg taken), 149·5 ± 0·5 mg (150·0 mg taken).

Sensitivity

The molar absorptivity is 3 l.mole^{-1}.cm^{-1} at 410 nm. The minimum amount detectable (Sandell sensitivity[14]) is 260 $\mu g/cm^2$.

Acknowledgement—The authors wish to thank Mrs. D. Nemoda for very valuable technical assistance, and the Laboratory of Physical Chemistry for use of its recording spectrophotometer.

Boris Kidrič Institute of Nuclear Sciences
Vinča, Yugoslavia

Z. DIZDAR
Z. IDJAKOVIĆ

Summary—A spectrophotometric method for the determination of milligram quantities of dimethyl sulphoxide in aqueous solutions has been developed. The method is based on the medium effect on the visible absorption spectra of metal salt solutions. Out of several compounds investigated, iron(III) alum was chosen as most suitable for this purpose. Beer's law is obeyed for dimethyl sulphoxide concentrations up to 20 mg/ml at 410 nm. Dimethyl sulphone does not interfere and dimethyl sulphide can be tolerated in amounts up to 25% of the sulphoxide present. Possible interferences caused by metal cations can be avoided by passing the sample through a cation-exchanger before adding the reagent. The molar absorptivity is 3 l.mole^{-1}.cm^{-1} at 410 nm, and the average relative error ±0·5%.

Zusammenfassung—Ein spektrophotometrisches Verfahren zur Bestimmung von Milligrammengen Dimethylsulfoxid in wäßrigen Lösungen wurde entwickelt. Es beruht auf dem Mediumeffekt auf die sichtbaren Absorptionsspektren von Metallsalzlösungen. Unter verschiedenen untersuchten Verbindungen wurde Eisen(III)-alaun als für diesen Zweck am besten geeignet ausgewählt. Bei 410 nm gilt das Beersche Gesetz für Dimethylsulfoxid-Konzentrationen bis höchstens 20 mg/ml. Dimethylsulfon stört nicht und Dimethylsulfid kann in Mengen bis 25% des Sulfoxids vorhanden sein. Mögliche Störungen durch Metall-Kationen können vermieden werden, wenn man die Probe vor Zugabe des Reagens durch einen Kationenaustauscher laufen läßt. Der molare Extinktionskoeffizient beträgt 3 l mol^{-1} cm^{-1} bei 410 nm, der mittlere relative Fehler ±0,5%.

Résumé—On a élaboré une méthode spectrophotométrique pour le dosage de quantités de diméthylsulfoxyde de l'ordre du milligramme en solutions aqueuses. La méthode est basée sur l'effet du milieu sur les spectres d'absorption dans le visible de solutions de sels métalliques. Parmi plusieurs composés étudiés, on a choisi l'alun de fer(III) comme convenant le mieux à cet usage. La loi de Beer est suivie pour des concentrations en diméthylsulfoxyde allant jusqu'à 20 mg/ml à 410 nm. La diméthylsulfone ne gêne pas, et le sulfure de diméthyle peut être toléré en quantités allant jusqu'à 25% du sulfoxyde présent. On peut éviter les interférences possibles causées par des cations métalliques en passant l'échantillon sur un échangeur de cations avant addition du réactif. Le coefficient d'absorption moléculaire est de 3 l.mole^{-1}.cm^{-1} à 410 nm, et l'erreur relative moyenne est de ±0,5%.

REFERENCES

1. T. B. Douglas, *J. Am. Chem. Soc.*, 1964, **68**, 1072.
2. L. H. Krull and M. Friedman, *J. Chromatog.*, 1967, **26**, 336.
3. G. Aravamudan and D. Venkappayya, *Talanta*, 1968, **15**, 704.
4. D. Barnard and K. R. Hargrave, *Anal. Chem. Acta*, 1951, **5**, 536.
5. E. Glynn, *Analyst*, 1947, **72**, 248.
6. S. Allenmark, *Acta Chem. Scand.*, 1966, **20**, 910.
7. C. A. Streuli, *Anal. Chem.*, 1958, **30**, 997.
8. D. C. Wimer, *ibid.*, 1958, **30**, 2060.
9. A. Fratiello, R. E. Lee, V. M. Nishida and R. E. Schuster, *J. Chem. Phys.*, 1967, **47**, 4951.
10. V. Gutmann and L. Hübner, *Monatsh. Chem.*, 1961, **92**, 1261.
11. Z. Dizdar and Z. Idjaković, unpublished work.
12. D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 1965, 649.
13. I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, 1962, **1**, 189.
14. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, 2nd Ed., p. 47. Interscience, New York, 1950.

Talanta, 1972, Vol. 19, pp. 1222 to 1226. Pergamon Press. Printed in Northern Ireland

Light-scattering, X-ray diffraction, elemental analysis and infrared spectrophotometry characterization of chitosan, a chelating polymer

(*Received* 30 *September* 1971. *Accepted* 16 *December* 1971)

THE CHELATING properties of chitosan have been described previously. The separation of transition metals from ammonium, thallium, alkali and alkaline-earth metals which cannot form co-ordination complexes with the polymer has been reported. It was pointed out that the collection rate of the first row transition metal ions follows the Irving and Williams series. Moreover, complexing agents were necessary to perform elutions from chitosan chromatographic columns. In several cases the adsorption of transition metal ions on chitosan is accompanied by the formation of intense colours, suggesting the occurrence of chemical bonding.[1–4]

The role of the free amino group $-NH_2$ in the interaction of cations with chitosan was confirmed when a study was made of solutions of chitosan in formic or acetic acids. Dissolution is made possible by the formation of $-NH_3^+$ groups: the $-NH_2$ groups are protonated, hindering the formation of a dative bond to a transition metal ion as shown by polarographic measurements.[4]

There is scarce information in the literature on the physical properties of chitosan and the present paper describes the correlation of the chromatographic behaviour of chitosan with physico-chemical data of particular interest in the technology of its preparation and use.

Data on chitin are more abundant, particularly X-ray diffraction studies.[9–11] The present work is limited to powders as at the present time there is no mean of isolating or obtaining a fibre or a crystal; artificial membranes are useful for infrared spectrophotometry only, as they are amorphous.[12]

EXPERIMENTAL

Cation-treated polymer

A 200-mg portion of chitosan was shaken for 30 min with 50 ml of a 0·044*M* solution of a metal sulphate or chloride. These concentrations are 100-fold higher than those currently used for chromatographic purposes and they were used to obtain clear X-ray and infrared records.

Instrumentation

Light-scattering measurements were carried out at 25° in pure benzene with a Model 42000 Sofica photometer equipped with cylindrical cells. The instrument was set to zero with dust-free benzene having a Rayleigh ratio $R_{90} = 16 \cdot 3 \times 10^{-6}$ at 546 nm. The refractive index increment d*n*/d*c* in 8·5% formic acid + 0·5*M* sodium formate at 25° was determined with a Brice–Phoenix Model BP-2000 V differential refractometer at 546 nm. All the glass equipment was cleaned by washing in a Thurmond apparatus,[13] and solutions were centrifuged at 15000 rpm for 2 hr. Infrared spectra were recorded with a Model 225 Perkin–Elmer spectrophotometer. X-Ray diffraction spectra were taken with a Nonius quadruple Guinier-De Wolff camera, with a quartz curved-crystal monochromator and a double cylinder camera of the Guinier-Jagodzinski type with a bent Johansson monochromator. Copper K_α radiation was used. Elemental analysis was carried out with an automatic F & M Hewlett–Packard analyser, with *N*-actylglucosamine as reference. Metals were measured with a Perkin–Elmer 305 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Light-scattering

The refractive index increments were measured at four distinct concentrations of chitosan in 8·5% formic acid + 0·5*M* sodium formate and at the two wave-lengths 436 and 546 nm; from the results the value d*n*/d*c* = 0·174 ml/g was obtained. Where chitosan solutions in formic acid are concerned, $-NH_3^+$ groups are responsible for the polyelectrolyte behaviour of the polymer, the $HCOO^-$ counter-ions being free to move.

At high concentrations, the polyelectrolyte molecules are close together and the counter-ions do not leave the molecular domain. At lower concentrations counter-ions diffuse away from the polymer molecules. The effective charge increases and the structure becomes more extended: sodium formate was added to the solvent to reduce this polyelectrolyte effect.

For each chitosan concentration, the light scattering was measured and the value C/I *vs.* $\sin^2 \theta/2 + 500\,C$ was plotted (according to Zimm[14]), in Fig. 1. The form of the graph indicates a degree of polydispersion as reported previously.[4] The extrapolated average molecular weight value was $1 \cdot 2 \times 10^6$.

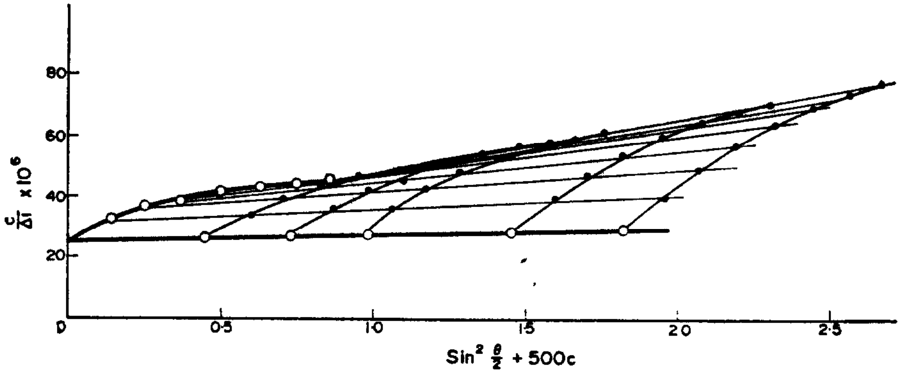


FIG. 1.—Light-scattering measurements on chitosan in formic acid (according to Zimm[14]).

Elemental analysis

In Table I results are reported for the nitrogen content of chitin and chitosan prepared under slightly different conditions (differing compositions of the deacetylation mixtures), derived from the method of Broussignac. Chitosan has the higher nitrogen content, which does not vary with the mode of preparation.

As shown in Table II there is a correlation between the nitrogen content and the capacity for

TABLE I.—ELEMENTAL ANALYSIS OF CHITOSAN SAMPLES, CHITIN AND DIETHYLAMINOETHYLCELLULOSE
(*N*-acetylglucosamine reference.)

Polymer	C	H	N
Chitosan (1st prep.)	40·0	6·8	7·4
Chitosan (2nd prep.)	39·7	6·2	7·4
Chitosan (3rd prep.)	39·8	6·1	7·3
Chitin	43·5	6·1	6·3
N-Acetylglucosamine	43·5	7·2	6·3
DE cellulose and PAB cellulose			1·2*

* Certified by Whatman and Bio-Rad.

TABLE II.—PERCENTAGE COLLECTION ON CHITOSAN, CHITIN AND CELLULOSE POWDERS
200 mg of polymer from 50 ml of 0·44 mM solutions, after one hour stirring. Chitosan and chitin 100–200 mesh; Whatman DE 11 and Bio-Rad PAB celluloses.

Ion	Chitosan	Chitin	DE Cel.	PAB Cel.
pH = 6				
Nickel	72	8	27	0
Copper	86	38	81	12
Zinc	77	22	86	16
Arsenic	25	0	10	0
Mercury	100	57	30	21
Lead	95	36	86	24
pH = 2·5				
Nickel	28	4	4	0
Copper	2	15	3	0
Zinc	22	0	0	0
Arsenic	100	0	10	0
Mercury	98	12	72	7
Lead	26	5	5	0

TABLE III.—OBSERVED *d* VALUES (Å) FOR CHITOSAN AND CATION-TREATED CHITOSAN

Chitosan	Chitosan +CuSO$_4$	Chitosan CuCl$_2$	Chitosan CdSO$_4$	Chitosan CdCl$_2$
8·49	6·99	5·65	9·01	9·42
4·46	6·37	5·41	5·07	5·11
3·02	5·32	2·74	4·36	4·40
2·48	4·44	2·55	3·01	2·45
2·27	3·90	2·38	2·47	2·28
2·06	3·18	2·24	2·27	2·09
1·90	3·01		2·17	1·91
1·86	2·91		1·90	1·87
	2·66		1·86	
	2·60			
	2·50			
	2·44			
	2·39			
	2·35			
	2·25			
	2·17			
	2·13			
	2·08			
	2·01			
	1·95			
	1·90			
	1·86			
	1·80			
	1·73			
	1·59			
	1·55			
	1·53			
	1·49			
	1·42			

collecting transition metal ions, indicating that the nitrogen atom is the main site of attachment. Of course contributions of other atoms are also involved as well as steric configurations and surface areas. Chitosan is much faster than other polymers, for instance the percentages for Ni and Zn in Table II are already reached after 10 minutes, while DE Cellulose after 10 minutes collects 22% Ni and 10% Zn only, at pH 6.

X-Ray diffraction and infrared spectrophotometry

The diffraction patterns of chitin and chitosan show some structural resembalance between the two polymers. The patterns for chitosan treated with copper sulphate and copper chloride reveal new sharp bands indicating a new highly crystalline structure, as presented in Table III. It is a well-known fact that when a matrix substance crystallizes with a "solute" additive, one can observe either a matrix lattice parameter alteration, or the formation of a new crystalline phase which is characterized by new bands in the X-ray diffraction pattern, the latter case occurring when the "solute" atoms occupy well-defined positions in the matrix lattice.

Copper ions occupy definite and fixed positions in the chitosan lattice and a chemical bond is established between the chitosan nitrogen atoms and the copper ions. Of course there is also a contribution by the hydroxyl groups. An anionic component is not excluded, as it is known that chitosan sulphate is crystalline. Chitosan treated with copper chloride yields more diffuse X-ray diffraction patterns, but this is due to a partial collapse of the grains at the lower pH.

The same trend is not observed in the X-ray diffraction patterns recorded for chitosan treated with other metal ions, *e.g.*, cadmium. Although the cadmium ions are held by dative bonds, they are introduced into the chitosan without altering the crystal structure (Table III). Should a physical adsorption occur, a less ordered chitosan structure would be observed; on the contrary a faint new band appears.

The infrared spectra for chitosan treated with various metal ions confirm that copper interacts more strongly than other ions. The whole spectrum is altered, instead of only the region around

1600 cm^{-1} as observed with certain other ions. Complexation of copper by the monomer (glucosamine) has been reported[15] and adsorption of copper on chitosan has been observed in chemical oceanography studies.[16,17]

The crystallinity of chitosan powder is not lost during chromatography. X-Ray diffraction studies on samples taken from the tops of the columns which had been used for the adsorption of copper from 0·44 m*M* solutions and subsequent elution with 0·01*M* EDTA show that the crystallinity improves as the number of cycles increases. This is accompanied by an increase in the amount of EDTA solution necessary to elute the same amount of copper, as shown in Table IV.

TABLE IV.—RECYCLING OF CHITOSAN COLUMNS (10 ml 0·44 m*M* copper sulphate and 100 ml of water, countercurrent at 3 ml/min).

Cycle no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Column, *cm*	7·5*	7·3	6·5	6·3	6·3	6·2	5·8	6·0	6·2	6·4	6·1	6·0	6·2	6·5
0·01*M* EDTA, ml	41	41	41	46	50	49	51	53	53	54	60	62	67	69

* The variation in height is due to application of pressure by a peristaltic pump. Whatman precision columns were used.

CONCLUSIONS

It is clear that chitosan used so far for chromatography of inorganic compounds is a macromolecule of average molecular weight 1·2 × 10^5 and that selected deacetylation procedures on chitin from crab shells do not lead to extended degradation of the polymer.

It is also verified that chitosan adsorbs transition metal ions because of its high nitrogen content (higher that 7%). On the other hand the limitations of cellulosic exchangers in aqueous solutions are a recognized fact. The change in the infrared spectrum in the amino-group region supports the idea of a chemical bond between the macromolecule and the cation.

Chitosan also reacts with complex anions such as metavanadate, molybdate, tungstate and possibly hexachloroplatinate and tetrachloroaurate.[4]

On repeated use in a chromatographic column, the crystallinity of chitosan is not lost, and in the case of copper it improves.

These results encourage the use of chitosan in chromatography, especially for the isolation of trace metals. Moreover ligand-exchange chromatography is at present confined to the use of copper-treated iminodiacetic acid resin (Chelex 100 or Dowex A 1), that has the limitations of leakage of copper ions, considerable shrinking and retention of magnesium. Ligand-exchange chromatography has also been carried out on cation-treated celluloses in organic solvents.[18] Chitosan may be recommended for this type of chromatography, because the metal ions on the polymer are available for interaction with ligands.

Acknowledgements—This work was performed under the auspices of the National Research Council of Italy (Contract No. 70.01602/22) and of the International Atomic Energy Agency, Vienna (Contract No. 895/RI/RB). The Authors are grateful to the NRC Laboratory of Photochemistry and High Energy Radiations, Bologna, for permission to use the Perkin–Elmer 225 I.R. spectrophotometer.

G. Ciamician" Chemical Institute
University of Bologna
Via Selmi 2, Bologna 40126, Italy

RICCARDO A. A. MUZZARELLI
ADELE FERRERO
MARIA PIZZOLI

Summary—Measurements on chitosan, which is used as a selective chromatographic support in inorganic chromatography, show that its molecular weight is 1·2 × 10^5, the nitrogen content is 7·4%, and its crystalline structure is not lost after adsorption of metal ions, which are co-ordinated with the nitrogen atoms of the —NH_2 groups of the polymer. Chitosan treated with copper sulphate exhibits a new crystal structure and a distinctive infrared spectrum, is quite stable and does not shrink, and is proposed as a chromatographic support for ligand-exchange chromatography.

Zusammenfassung—Messungen an Chitosan, das als selektiver chromatographischer Träger bei der anorganischen Chromatographie verwendet wird, ergaben ein Molekulargewicht von 1,2 · 10^5 und einen Stickstoffgehalt von 7,4%; seine Kristallstruktur geht nach Adsorption von Metallionen nicht verloren. Die Metallionen sind mit den Stickstoffatomen der —NH_2-Gruppen am Polymeren koordiniert. Mit Kupfersulfat behandeltes Chitosan zeigt eine neue Kristallstruktur und ein anderes Infrarotspektrum, ist recht stabil, schrumpft nicht und wird als chromatographischer Träger zur Ligandenaustauschchromatographie vorgeschlagen.

Résumé—Les mesures sur le chitosane, qui est utilisé comme support chromatographique sélectif en chromatographie minérale, montrent que son poids moléculaire est 1,2 × 10^5, la teneur en azote est 7,4%, et sa structure cristalline n'est pas perdue après adsorption d'ions métalliques, qui sont coordonnés avec les atomes d'azote des groupes —NH_2 du polymère. Le chitosane traité avec le sulfate de cuivre montre une nouvelle structure cristalline et un spectre infra-rouge particulier, il est tout à fait stable et ne se contracte pas, et on le propose comme support chromatographique pour la chromatographie d'échange de ligands.

REFERENCES

1. R. A. A. Muzzarelli, Natural Chelating Polymers, Pergamon Press Ltd., Oxford, 1973.
2. R. A. A. Muzzarelli, U.S.A. Patent 3,635,818 (1972) (Italian priority 1968).
3. R. A. A. Muzzarelli and O. Tubertini, *Talanta*, 1969, **16**, 1571.
4. R. A. A. Muzzarelli, *Anal. Chim. Acta*, 1971, **54**, 133.
5. R. A. A. Muzzarelli, R. Rocchetti and G. Marangio, *J. Radioanal. Chem.*, 1972, **10**, 17.
6. R. A. A. Muzzarelli and B. Spalla, *ibid.*, 1972, **10**, 27.
7. R. A. A. Muzzarelli, G. Raith and O. Tubertini, *J. Chromatogr.*, 1970, **47**, 414.
8. R. A. A. Muzzarelli and O. Tubertini, *Mikrochim. Acta*, 1971, 890.
9. S. E. Darmon and K. M. Rudall, *Disc. Faraday. Soc*, 1950, 251.
10. M. Falk, D. G. Smith, J. McLachlan and A. G. McInnes, *Can. J. Chem.*, 1966, **44**, 2269
11. N. E. Dweltz, J. R. Colvin and A. G. McInnes, *ibid.*, 1968, **46**, 1513.
12. R. A. A. Muzzarelli and A. Isolati, in preparation.
13. C. D. Thurmond, *J. Polymer Sci.*, 1952, **8**, 607.
14. B. H. Zimm, *J. Chem. Phys.*, 1948, **16**, 1093.
15. S. M. Manskaya, T. V. Drozdova and N. P. Emelyanova, *Pochvovedenie*, 1958, 41.
16. R. A. A. Muzzarelli and L. Sipos, *Talanta*, 1971, **18**, 853.
17. R. A. A. Muzzarelli, *Rev. Intl. Oceanog. Medicale*, 1971, **21**, 93.
18. R. A. A. Muzzarelli, A. Ferrero and O. Tubertini, *Analyst*, 1969, **94**, 616.

Talanta, 1972, Vol. 19, pp. 1226 to 1231. Pergamon Press. Printed in Northern Ireland

A simple non-selective detector for gas-phase chromatography, using the measurement of reflected microwave power

(*Received* 10 *December* 1971. *Accepted* 8 *February* 1972)

THE CONSIDERABLE volume of work[1-9] on the use of microwave-excited discharges as detectors in gas-phase chromatography has been exclusively concerned with their capabilities as sources of selective spectral emission. The emission produced as the eluates are fragmented and excited in the discharge is usually detected with a monochromator, photomultiplier and electronic read-out system. Emission at particular wavelengths is found to be characteristic of certain atoms in the original compounds. One disadvantage of this type of system is the difficulty, even with very fast-scan monochromators or when using a polychromator, of detecting and determining all the species eluted from the column, with only one sample injection. A non-destructive, non-selective detector such as the katharometer, placed between the column and the discharge, would increase the amount of necessary apparatus and dead volume.

This communication describes a non-selective detector which can be used simultaneously with the emissive detector. The detector responds to nanogram quantities of all substances tested and requires

sind mit den Stickstoffatomen der —NH$_2$-Gruppen am Polymeren koordiniert. Mit Kupfersulfat behandeltes Chitosan zeigt eine neue Kristallstruktur und ein anderes Infrarotspektrum, ist recht stabil, schrumpft nicht und wird als chromatographischer Träger zur Ligandenaustauschchromatographie vorgeschlagen.

Résumé—Les mesures sur le chitosane, qui est utilisé comme support chromatographique sélectif en chromatographie minérale, montrent que son poids moléculaire est 1,2 × 10^6, la teneur en azote est 7,4%, et sa structure cristalline n'est pas perdue après adsorption d'ions métalliques, qui sont coordonnés avec les atomes d'azote des groupes —NH$_2$ du polymère. Le chitosane traité avec le sulfate de cuivre montre une nouvelle structure cristalline et un spectre infra-rouge particulier, il est tout à fait stable et ne se contracte pas, et on le propose comme support chromatographique pour la chromatographie d'échange de ligands.

REFERENCES

1. R. A. A. Muzzarelli, Natural Chelating Polymers, Pergamon Press Ltd., Oxford, 1973.
2. R. A. A. Muzzarelli, U.S.A. Patent 3,635,818 (1972) (Italian priority 1968).
3. R. A. A. Muzzarelli and O. Tubertini, *Talanta*, 1969, **16**, 1571.
4. R. A. A. Muzzarelli, *Anal. Chim. Acta*, 1971, **54**, 133.
5. R. A. A. Muzzarelli, R. Rocchetti and G. Marangio, *J. Radioanal. Chem.*, 1972, **10**, 17.
6. R. A. A. Muzzarelli and B. Spalla, *ibid.*, 1972, **10**, 27.
7. R. A. A. Muzzarelli, G. Raith and O. Tubertini, *J. Chromatogr.*, 1970, **47**, 414.
8. R. A. A. Muzzarelli and O. Tubertini, *Mikrochim. Acta*, 1971, 890.
9. S. E. Darmon and K. M. Rudall, *Disc. Faraday. Soc*, 1950, 251.
10. M. Falk, D. G. Smith, J. McLachlan and A. G. McInnes, *Can. J. Chem.*, 1966, **44**, 2269
11. N. E. Dweltz, J. R. Colvin and A. G. McInnes, *ibid.*, 1968, **46**, 1513.
12. R. A. A. Muzzarelli and A. Isolati, in preparation.
13. C. D. Thurmond, *J. Polymer Sci.*, 1952, **8**, 607.
14. B. H. Zimm, *J. Chem. Phys.*, 1948, **16**, 1093.
15. S. M. Manskaya, T. V. Drozdova and N. P. Emelyanova, *Pochvovedenie*, 1958, 41.
16. R. A. A. Muzzarelli and L. Sipos, *Talanta*, 1971, **18**, 853.
17. R. A. A. Muzzarelli, *Rev. Intl. Oceanog. Medicale*, 1971, **21**, 93.
18. R. A. A. Muzzarelli, A. Ferrero and O. Tubertini, *Analyst*, 1969, **94**, 616.

Talanta, 1972, Vol. 19, pp. 1226 to 1231. Pergamon Press. Printed in Northern Ireland

A simple non-selective detector for gas-phase chromatography, using the measurement of reflected microwave power

(*Received* 10 *December* 1971. *Accepted* 8 *February* 1972)

THE CONSIDERABLE volume of work[1-9] on the use of microwave-excited discharges as detectors in gas-phase chromatography has been exclusively concerned with their capabilities as sources of selective spectral emission. The emission produced as the eluates are fragmented and excited in the discharge is usually detected with a monochromator, photomultiplier and electronic read-out system. Emission at particular wavelengths is found to be characteristic of certain atoms in the original compounds. One disadvantage of this type of system is the difficulty, even with very fast-scan monochromators or when using a polychromator, of detecting and determining all the species eluted from the column, with only one sample injection. A non-destructive, non-selective detector such as the katharometer, placed between the column and the discharge, would increase the amount of necessary apparatus and dead volume.

This communication describes a non-selective detector which can be used simultaneously with the emissive detector. The detector responds to nanogram quantities of all substances tested and requires only a simple modification to the reflected-power meter associated with the usual microwave power supply.

EXPERIMENTAL

The system used is in principle the same as that described previously[6] except that a Beckman DU monochromator replaced the Hilger and Watts D292 monochromator.

An Evans Electroselenium Limited (EEL) model 245 microwave generator was used as the microwave power supply. The method of detection consisted of measuring the changes in the reflected microwave power produced by the chromatographic eluent entering the microwave discharge. The EEL 245 generator is ideally suited in this respect because it contains a built-in reflected-power meter and also the magnetron power supply is current-stabilized, which reduces the background noise. The output of the reflected-power meter was connected, *via* a coaxial cable and a backing-off system to a multirange Servo scribe recorder (see Fig. 1). A damping capacitor (40 μF) was connected across the recorder terminals to decrease the short-term noise on the background signal.

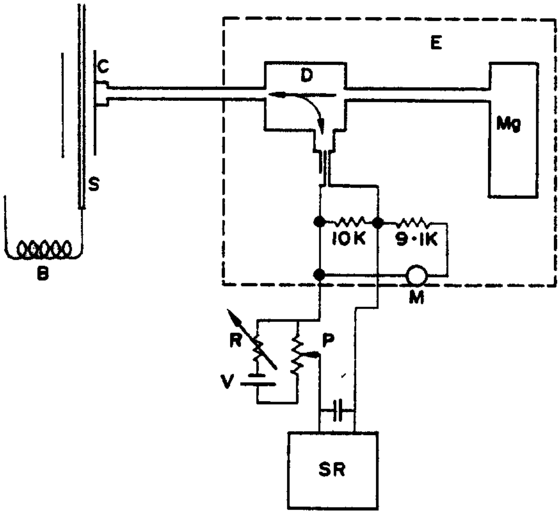


FIG. 1.—Experimental arrangement.
Mg—magnetron valve, D—directional coupler, C—cavity, B—column, S—silica tube, M—meter, E—EEL microwave generator, V—4·5-V battery, R—variable resistance (up to 1 MΩ), P—10 K potentiometer, SR—Servoscribe recorder.

With the discharge operating at 90 W of microwave power a background signal of *ca* 200 mV was produced by the reflected-power meter. When this voltage was backed-off so that it could be displayed on the 10-mV range of the recorder, a baseline with a drift of less than 3mV/hr and a low noise level was obtained. When an eluate passed through the discharge, the microwave power was coupled more efficiently, decreasing the reflected power and thus producing a signal peak.

The system conditions were optimized by using 5-μl injections of a mixture of 2.12% propene and 1·25% n-butene in nitrogen into a 1-m Porapak S column at 150°. The effect of microwave power variation when using an argon flow-rate of 3·5 l/hr is shown in Fig. 2, together with those for oxygen and nitrogen at the same flow-rate on a 3-m molecular sieve column at 25° (the maximum power obtainable from the microwave generator is limited to 90 W). The variation in the reflected-power background was also measured and found to be linear with respect to applied power. The variation of noise proved difficult to measure accurately, as signal detection was variable and limited by drift. However, no appreciable increase in noise was found at higher powers and 90 W was used throughout this work.

The effect of variations in flow-rate for the same substances is shown in Figs. 3 and 4. The effect of flow-rate changes is considerable and is *ca.* twice as great as for the emissive system alone (Fig. 4). However, the background drift was found to increase at slower flow-rates, probably as a result of increased instability in the flow-rate. Hence a non-optimum, but convenient, flow-rate of 3.5 l./hr was used for the sensitivity studies.

The reflected power detector could be used simultaneously with, and independently of, the emissive detector described in previous studies. Hence the method chosen to measure the ranges of linearity

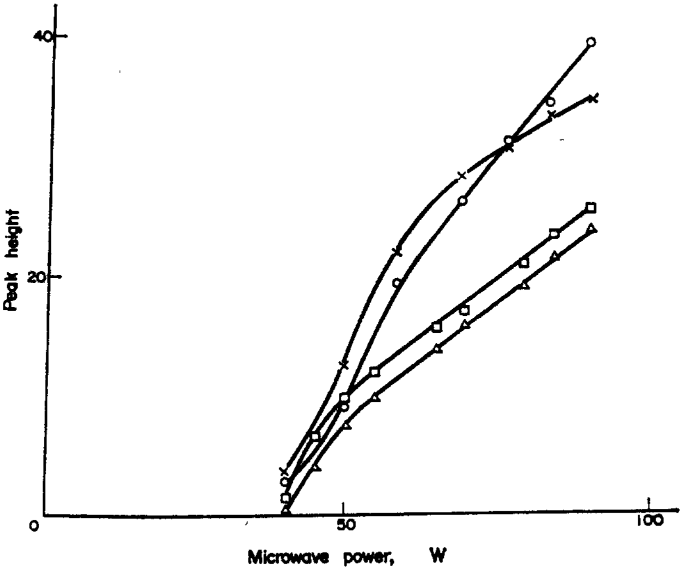


FIG. 2.—The effect of microwave power on detector response.
○—Oxygen; ×—nitrogen; □—propene; △—n-butene.

for a series of organic compounds was to compare the responses of these two systems; the emissive detector was set to record the atomic carbon emission at 247·9 nm. The response of the emissive detector at this wavelength had already been shown to be linear for the compounds used. A range of very small quantities ($\leqslant 1$ μl) of pure compounds were injected and the response of the two detector systems was recorded simultaneously. The linearity of response was established by plotting its response against that of the emissive detector.

From these results the approximate limits of detection were estimated and standard solutions of approximately these concentrations were made up and used to obtain more accurate figures. The

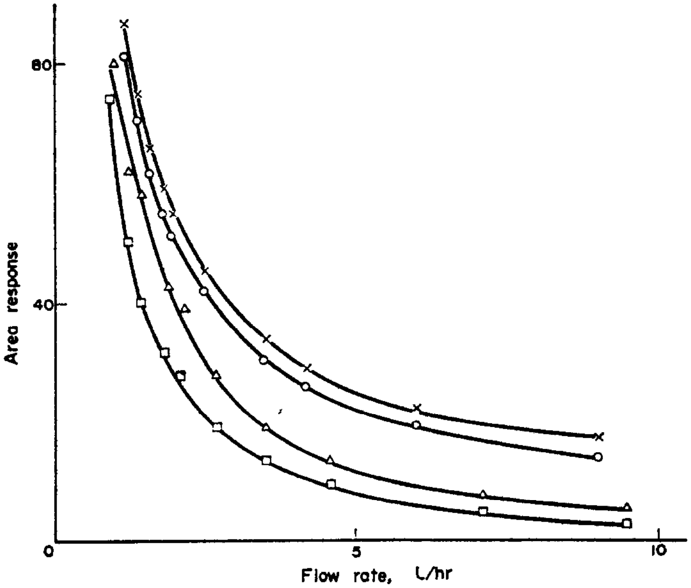


FIG. 3.—The effect of flow rate on detector response.
□—Propene; △—n-butene; ○—oxygen; ×—nitrogen.

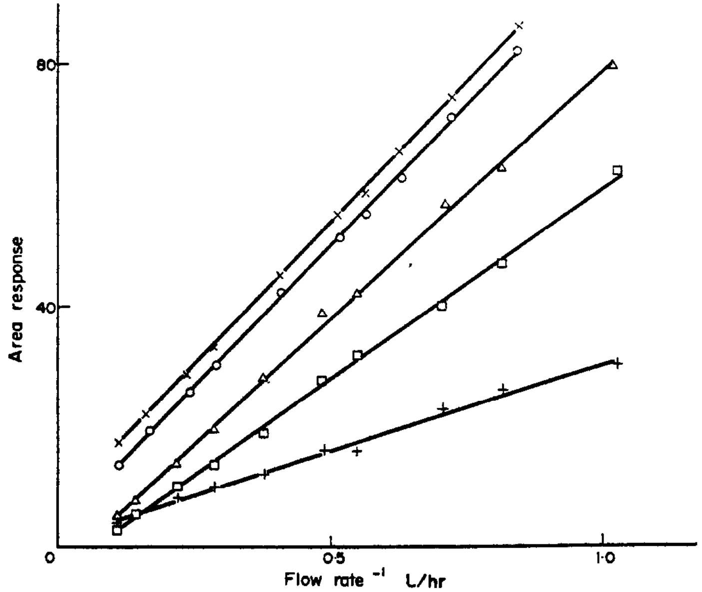


FIG. 4.—The variation of detector response with reciprocal of flow rate. ○—oxygen; ×—nitrogen; □—propene; △—n-butene; +—propene, with measurement of atomic carbon emission at 247·9 nm.

sensitivity to water was obtained in the same way by comparing it with the OH emission at 306.4 nm.

The response of the detector to a range of gases was measured directly, using 5-μl injections of the pure gases. For some gases, particularly nitrous oxide, oxygen and nitrogen impurities were observed and a correction was made, based on previously obtained sensitivities.

RESULTS AND DISCUSSION

A central position of the tube in the cavity was found to be optimum, and it was important to keep the tube position unchanged during operation, otherwise changes in reflected power occurred. Carbon deposition was generally not a problem at the sample levels used (less than 10 μg/sec) and the usable lifetime of the silica tubing was similar to that when used with the emissive detector.[8]

TABLE I.—DETECTOR RESPONSE TO SELECTED ORGANIC COMPOUNDS.

Compound	Column	Retention time, *min*	Range of linearity,* *ng/sec*	Limit of detection, *ng/sec*
Acetone	P	2·96	2–1000	2·1
Diethyl ether	P	3·25	2–1000	2·8
Ethanol	P	1.92	2–1000	1·3
Isopropanol	P	3·93	2–1000	1·3
n-Propanol	P	5·66	2–1000	1·4
Toluene	C	2·91	2–2000	1·4
Ethyl iodide	C	0.92	6–600	5.8
Carbon tetrachloride	C	1·25	2–1000	8·0
Chloroform	C	1.05	2–1000	5·7
n-Propyl bromide	C	0·90	2–1000	3·3
Methyl cyanide	C	0.33	2–1000	3·6
Thiophen	C	1·30	2–1000	2.3

C = 0·7-m Chromosorb 101 column.
P = 1-m Porapak S column.
Both columns were used at 150°C with an argon flow-rate of 3·6 l./hr.
* Approximate values.

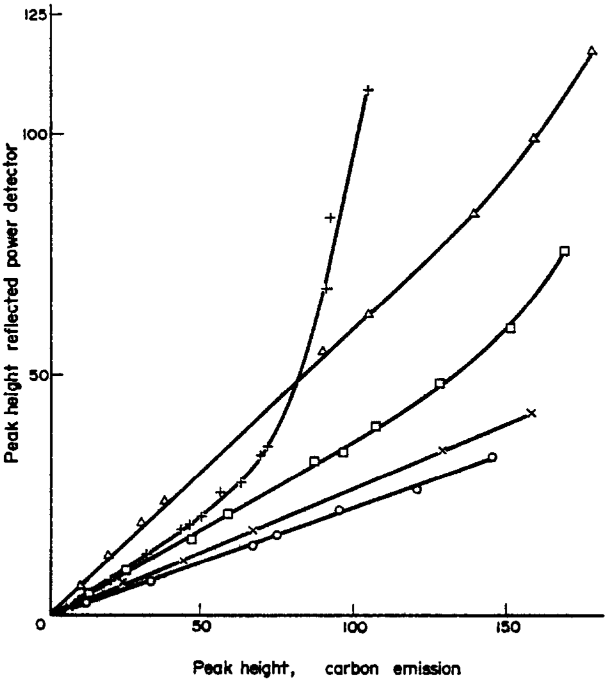


FIG. 5.—The relative responses of the reflected-power detector and the emissive detector at 247·9 nm.
+—Ethyl iodide; ○—methyl cyanide; ×—toluene; □—carbon tetrachloride; △—n-propyl bromide.

TABLE II.—DETECTOR RESPONSE TO A RANGE OF PERMANENT GASES

Gas	Temperature °C	Column	Retention time, *min*	Limit of detection, *ng/sec*
Oxygen	25	M	1·15	3·8
Nitrogen	25	M	1·35	2·8
Helium	25	M	1.00	8.8
Hydrogen	25	M	1·03	0.3
Carbon monoxide	50	M	2·02	3·4
Carbon dioxide	50	P	0·73	4·2
Nitrous oxide	50	P	1·25	2·4
Methane	50	P	0·30	1·0
Ethylene	50	P	1.21	0·9
Propylene	150	P	0·52	0·9
n-Butene	150	P	1·01	1.1

M = 3-m Molecular Sieve column.
P = 1-m Porapak column.

The limits of detection and ranges of linearity obtained for the organic compounds and gases are shown in Tables I and II. A comparison with the emissive detector is shown in Fig. 5. The range of linearity was greater than 500 for all the compounds investigated except ethyl iodide which was about 100. The limits of detection for all compounds and gases were quite similar, that is nanogram quantities, and the detector exhibited a particularly good response to hydrogen and to a lesser extent to hydrocarbons. No special sensitivity to N, S, O, I, Cl or Br compounds was found. The limits of detection for organic compounds were *ca.* 10–20 times poorer than those for carbon emission measurements with the emissive detector.[9] However, the limits of detection for helium, hydrogen, oxygen and water are superior to those obtained by emission measurement.[1,9]

Department of Chemistry
Imperial College, London S.W.7.

R. M. Dagnall
M. D. Silvester
T. S. West
P. Whitehead

Summary—A non-selective detector is described which can be used in conjunction with the microwave-excited emissive argon plasma detector. The mode of operation is based on the measurement of reflected power and its use is demonstrated with respect to a range of component vapours and permanent gases. The limit of detection for nearly all the species investigated is in the nanogram range and the detector responded to all compounds examined.

Zusammenfassung—Ein nichtselektiver Detektor wird beschrieben, der in Verbindung mit dem mikrowellen-erregten Argon-plasma-Emissionsdetektor verwendet werden kann. Die Arbeitsweise beruht auf der Messung der reflektierten Leistung; die Verwendung des Detektors wird an verschiedenen Dämpfen und permanenten Gasen demonstriert. Die Nachweisgrenze für fast alle untersuchten Spezies liegt im Nanogrammbereich; der Detektor sprach auf alle untersuchten Verbindungen an.

Résumé—On décrit un détecteur non sélectif qui peut être utilisé conjointement au détecteur à plasma d'argon émissif excité par microondes. Le mode d'action est basé sur la mesure de la puissance réfléchie et son usage est démontré par rapport à une gamme de vapeurs élémentaires et de gaz permanents. La limite de détection pour presque toutes les espèches étudiées est dans le domaine du nanogramme et le détecteur a répondu à tous les composés examinés.

REFERENCES

1. A. J. McCormack, S. C. Tong and W. D. Cooke, *Anal. Chem.*, 1965, **37**, 1470.
2. C. A. Bache and D. J. Lisk, *ibid.*, 1965, **37**, 1477.
3. *Idem, ibid.*, 1966, **38**, 783.
4. *Idem, ibid.*, 1966, **38**, 1757.
5. *Idem, ibid.*, 1967, **39**, 787.
6. H. A. Moye *ibid.*, 1967, **39**, 1441.
7. R. M. Dagnall, S. J. Pratt, T. S. West and D. R. Deans, *Talanta*, 1969, **16**, 797.
8. *Idem., ibid.*, 1970, **17**, 1009.
9. R. M. Dagnall, T. S. West and P. Whitehead, *Anal. Chim. Acta*, in the press.

Talanta, 1972, Vol. 19, pp. 1231 to 1234. Pergamon Press. Printed in Northern Ireland

Selective detection of bismuth(III) and iron(II) ions with certain new reagents

(*Received* 10 *January* 1972. *Accepted* 17 *February* 1972)

This communication describes the analytical applications of certain organic compounds proposed as reagents for the selective detection of bismuth(III): isoperthiocyanic acid (I), tetraethylthiuram monosulphide (II), eosin (III) and mercurochrome (IV). Eosin and mercurochrome also give useful fluorescent colour reactions with iron(II).

detection for organic compounds were *ca.* 10–20 times poorer than those for carbon emission measurements with the emissive detector.[9] However, the limits of detection for helium, hydrogen, oxygen and water are superior to those obtained by emission measurement.[1,9]

Department of Chemistry
Imperial College, London S.W.7.

R. M. DAGNALL
M. D. SILVESTER
T. S. WEST
P. WHITEHEAD

Summary—A non-selective detector is described which can be used in conjunction with the microwave-excited emissive argon plasma detector. The mode of operation is based on the measurement of reflected power and its use is demonstrated with respect to a range of component vapours and permanent gases. The limit of detection for nearly all the species investigated is in the nanogram range and the detector responded to all compounds examined.

Zusammenfassung—Ein nichtselektiver Detektor wird beschrieben, der in Verbindung mit dem mikrowellen-erregten Argon-plasma-Emissionsdetektor verwendet werden kann. Die Arbeitsweise beruht auf der Messung der reflektierten Leistung; die Verwendung des Detektors wird an verschiedenen Dämpfen und permanenten Gasen demonstriert. Die Nachweisgrenze für fast alle untersuchten Spezies liegt im Nanogrammbereich; der Detektor sprach auf alle untersuchten Verbindungen an.

Résumé—On décrit un détecteur non sélectif qui peut être utilisé conjointement au détecteur à plasma d'argon émissif excité par microondes. Le mode d'action est basé sur la mesure de la puissance réfléchie et son usage est démontré par rapport à une gamme de vapeurs élémentaires et de gaz permanents. La limite de détection pour presque toutes les espèches étudiées est dans le domaine du nanogramme et le détecteur a répondu à tous les composés examinés.

REFERENCES

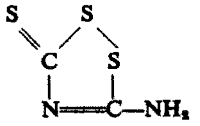
1. A. J. McCormack, S. C. Tong and W. D. Cooke, *Anal. Chem.*, 1965, **37**, 1470.
2. C. A. Bache and D. J. Lisk, *ibid.*, 1965, **37**, 1477.
3. *Idem*, *ibid.*, 1966, **38**, 783.
4. *Idem*, *ibid.*, 1966, **38**, 1757.
5. *Idem*, *ibid.*, 1967, **39**, 787.
6. H. A. Moye *ibid.*, 1967, **39**, 1441.
7. R. M. Dagnall, S. J. Pratt, T. S. West and D. R. Deans, *Talanta*, 1969, **16**, 797.
8. *Idem.*, *ibid.*, 1970, **17**, 1009.
9. R. M. Dagnall, T. S. West and P. Whitehead, *Anal. Chim. Acta*, in the press.

Talanta, 1972, Vol. 19, pp. 1231 to 1234. Pergamon Press. Printed in Northern Ireland

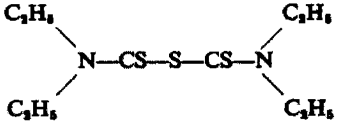
Selective detection of bismuth(III) and iron(II) ions with certain new reagents

(*Received* 10 *January* 1972. *Accepted* 17 *February* 1972)

THIS COMMUNICATION describes the analytical applications of certain organic compounds proposed as reagents for the selective detection of bismuth(III): isoperthiocyanic acid (I), tetraethylthiuram monosulphide (II), eosin (III) and mercurochrome (IV). Eosin and mercurochrome also give useful fluorescent colour reactions with iron(II).

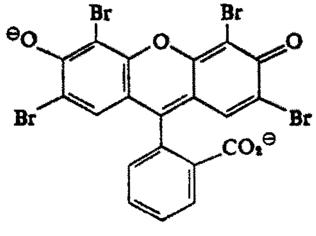


I

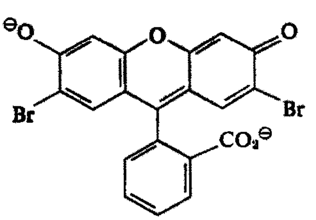


$$(C_2H_5)_2N{-}CS{-}S{-}CS{-}N(C_2H_5)_2$$

II



III



IV

Isoperthiocyanic acid, discovered by Wöhler,[1] has been a compound of controversial structure.[2] It has recently been shown to be 3-amino-5-thione-1,2,4-dithiazole (I).[3,4] No work has hitherto been reported on its analytical applications. It has now been observed that I dissolves in conc. sulphuric acid to give a stable yellow solution which reacts specifically with bismuth in presence of iodide, giving a deep red or intensely reddish-orange precipitate. With the exception of nitrite, no common anion or cation [including Sb(III) and As(III)] interferes. Nitrite, if present, should first be removed by treatment with sodium azide or sulphamic acid.[5] Like I, II reacts with bismuth in presence of iodide ions, giving a deep-orange precipitate. Only nitrite interferes. A 25% w/v alcohol solution of II is sold under the trade name of "Tetmosol".

Eosin and mercurochrome are important xanthene dyes. Both, when treated with bismuth and made alkaline with ammonia, give a bright and characteristic deep pink or reddish-pink precipitate. No other common anion or cation (except Pb) gives this result. Antimony(III) under identical conditions gives a light orange precipitate with a slightly pinkish tint, quite distinctive from that with bismuth. Because of their reaction with ammonia, Fe(II), Fe(III) and Cu(II) interfere.

Both III and IV, when treated with iron(II) and made alkaline with ammonia, give a highly fluorescent green precipitate. The reaction is specific for iron(II), and no interference is caused by iron(III) or by other common cations or anions.

EXPERIMENTAL

Reagents

Isoperthiocyanic acid solution (*A*). A 5% w/v solution in conc. sulphuric acid. I was obtained by the Seltzer and Considine method.[6]

Tetraethylthiuram monosulphide solution (*B*). A 5% w/v solution in acetone (prepared by diluting 20 ml of 25% w/v I.C.I. medicinal grade "Tetmosol" solution to 100 ml with acetone).

Eosin solution (*C*). A 0·5% w/v solution of the disodium salt in water.

Mercurochrome solution (*D*). A 0·3% w/v solution of the disodium salt in water.

Procedures

Bismuth with isoperthiocyanic acid. Place 2 drops of 2% potassium iodide solution on a spot plate, mix with it 1 drop of solution *A*, add 1 drop of test solution and again stir. Bismuth gives a deep red or intensely reddish-orange precipitate.

Limit of detection: 1 μg of bismuth: *limit of dilution*: 1:50,000.

Bismuth with tetraethylthiuram monosulphide. To 2 ml of 2% potassium iodide solution add 5 drops of solution *B*, followed by 1–2 ml of the test solution (containing 5–10 μg of bismuth). A deep reddish-orange precipitate indicates bismuth. Sometimes, generally in presence of large excess of potassium iodide, a transient blood-red precipitate forms which within seconds becomes intensely reddish-orange.

Bismuth with eosin or mercurochrome. To 2 ml of acidic test solution (containing >200 μg of bismuth) add 2–3 drops of solution *C* or *D*, and about 1 ml of conc. ammonia solution. A heavy, bright deep pink or reddish-pink precipitate indicates bismuth.

Iron(II) with eosin or mercurochrome. To 1–2 ml of the test solution, add 3–6 drops of solution

C or *D*, and 1–2 ml of conc. ammonia solution and shake the mixture thoroughly. In presence of iron(II) a brownish-orange or purple-orange precipitate with intense green fluorescence is formed. The fluorescence is so intense that a precipitate appears deep green with highly intense green fluorescence. Large quantities of copper(II) interfere.

Limit of detection: 3 μg/ml.

RESULTS AND DISCUSSION

The nature of products in the tests with I *and* II

I and II, like many other nitrogeneous organic bases, react with bismuth in presence of potassium iodide to form coloured products (double iodides) of general formula BiI_3. base. HI, which may be regarded as salts of the base with iodobismuthic acid, $H[BiI_4]$. The literature contains many examples of the "acid" character[7] of I, but only a few examples of its "basic" character are known.[6] The test for bismuth with I is an additional and unambiguous proof of its basic nature (*cf.* cinchonine, quinine, quinoline, *etc*[8]).

The bismuth tests with I and II are also specific for iodide. Nitrites, as usual, cause interference.

The nature of products in tests with III *and* IV

The characteristic coloured products in the bismuth test are likely to be "adsorption complexes" of the dyes with the bismuth hydroxide formed on addition of the ammonia. However, that ammonia may be involved in the constitution of the adsorption complexes is indicated by the fact that the test fails if sodium hydroxide is used in place of ammonia. The green fluorescent iron(II) precipitate is also presumed to be an "adsorption complex". This is confirmed by the fact that a similar product is obtained when a suspension of freshly prepared ferrous hydroxide [produced by treating an iron(II) solution with ammonia or sodium hydroxide] in water is mixed and shaken with a little eosin or mercurochrome solution.

Department of Chemistry
V.S.S.D. College
Kanpur-2, India

G. S. Johar

Summary—Isoperthiocyanic acid (3-amino-5-thione-1,2,4-dithiazole) (I), tetraethylthiuram monosulphide ("Tetmosol") (II), eosin (III), and mercurochrome (IV) are used as new qualitative reagents for bismuth. III and IV are also used for detection of iron(II). A conc. sulphuric acid solution of I, or an acetone solution of II, when treated with bismuth in presence of potassium iodide, gives a deep red or reddish-orange precipitate, characteristic of bismuth. Bismuth in presence of III or IV gives a heavy and characteristically bright deep-pink precipitate on addition of ammonia. With I, 1 μg of bismuth may be detected with a dilution limit of 1:50,000. Sb(III) and As(III) do not interfere in any of these tests. Iodides interfere only when I and II are used as reagents. Pb, Cu(II), and Fe(III) interfere with III and IV. I and II are also proposed as reagents for iodide; nitrites would interfere. III and IV, with iron(II) on addition of ammonia, produce a precipitate with highly intense green fluorescence. No other common cation [including Fe(III)] or anion interferes. The limit of detection is 3 μg/ml.

Zusammenfassung—Isosuperthiocyansäure (3-Amino-5-Thion-1,2,4-Dithiazol) (I), Tetraäthylthiuram Monosulphid ("Tetmosol") (II), Eosin (III) und Mercurochrom (IV) werden als neue qualitative Reagenzien für Wismuth benutzt. III und IV werden auch zur Feststellung von Eisen(II) benutzt. Eine konz. Schwefelsäurelösung von I oder eine Acetonlösung von II ergibt einen tiefroten oder rötlich-orangenen, für Wismuth charakteristischen Niederschlag, wenn mit Wismuth in Gegenwart von Kaliumjodid behandelt. Wismuth gibt bei Vorhandensein von III oder IV einen schweren und bei Zugabe von Ammoniak charakteristischen glänzenden, tiefrosa Niederschlag. Bei I kann kann bei einem Verdünnungsgrenzwert von 1:50,00 1 μg von Wismuth entdeckt werden. Sb(III) und As(III) stören in keinem dieser

Teste. Jodide stören nur, wenn I und II als Reagens benutzt werden. Pb, Cu(II) und Fe(III) stören mit III und IV I. und II werden auch als Reagens für Jodid vorgeschlagen: Nitrate würden sich störend auswirken. III und IV, mit Eisen(II) und Zusatz von Ammonia produzieren einen Niederschlag mit sehr intensiver Fluoreszenz. Kein anderes gewöhnliches Kation (einschliesslich Fe(III)) oder Anion stört. Der Grenzwert für Feststellung ist 3 μg/ml.

Résumé—On utilise l'acide isoperthiocyanique (3-amino 5-thione 1,2,4-dithiazole) (I), le monosulfure de tétraéthylthiurame ("Tetmosol") (II), l'éosine (III), et le mercurochrome (IV) comme nouveaux réactifs qual-i tatifs du bismuth. III et IV sont aussi utilisés pour la détection du fer(II). Une solution de I dans l'acide sulfurique concentré, ou une solution de II dans l'acétone, lorsqu'elle est traitée par le bismuth en présence d'iodure de potassium, donne une précipité rouge foncé ou rouge-orangé, caractéristique du bismuth. Le bismuth en présence de III ou IV donne un précipité dense et spécifiquement rose foncé vif par addition d'ammoniaque. Avec I, on peut détecter 1 μg de bismuth avec une limite de dilution de 1:50 000. Sb(III) et As(III) ne gênent dans aucun de ces essais. Les iodures gênent seulement lorsque I et II sont utilisés comme réactifs. Pb, Cu(II) et Fe(III) gênent avec III et IV. I et II sont aussi proposés comme réactifs de l'iodure; les nitrites gêneraient. III et IV, avec le fer(II) en plus de l'ammoniaque produisent un précipité de fluorescence verte extrêmement intense. Aucun autre cation [y compris le fer(III)] ou anion communs n'interfèrent. La limite de détection est de 3 μg/ml.

REFERENCES

1. A. Wöhler, *Ann. Phys.*, 1821, **69**, 273.
2. R. C. Elderfield, *Heterocyclic Compounds*, Vol. 7, p. 569. Wiley, New York, 1961.
3. A. Hordwik, *Acta Chem. Scand.*, 1961, **15**, 1186.
4. H. J. Emeléus, A. Haas and N. J. Shepperd, *J. Chem. Soc.*, 1963, 3165.
5. F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Ed., p. 329. Elsevier, Amsterdam, 1958.
6. R. Seltzer and W. Considine, *J. Org. Chem.*, 1970, **35**, 1665.
7. L. L. Bambas, *The Chemistry of Heterocyclic Compounds*, Vol. 4, p. 35. Interscience, New York, 1952.
8. F. J. Welcher, *Organic Analytical Reagents*, Vols. I–IV, Van Nostrand, New Jersey, 1947.

Talanta, 1972, Vol. 19, pp. 1235 to 1236. Pergamon Press. Printed in Northern Ireland

ANALYTICAL DATA

Polarography of Cd–malonate–oxalate complex

(*Received* 18 *November* 1971. *Accepted* 26 *January* 1972)

Little attention has been paid to the polarographic study of mixed ligand complexes. Schaap and McMasters[1] were the first to provide a logical extension of the method of DeFord and Hume[2] for the study of such mixed species. We have applied their method to the study of malonate–oxalate complexes of cadmium.

Since Cd^{2+} forms hexaco-ordinate complexes with oxalate and malonate individually,[1,3] there can be at most three mixed complex species, $Cd(XY_2)$, $Cd(XY)$ and $Cd(X_2Y)$.

$$M + iX + jY \rightleftharpoons MX_iY_j$$

The DeFord and Hume expression for $F_0(X)$ may be extended to give a new function F_{00}:

$$F_{00}(X, Y) = \text{antilog}\left[\frac{0{\cdot}434nF}{RT}\Delta E_{1/2} + \log\frac{I_M}{I_0}\right]$$

where the symbols have their usual significance.

From Leden's approach[4]

$$\begin{aligned} F_0(X, Y) = {} & \{\beta_{00} + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3\}[X]^0 \\ & + \{\beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2\}[X] \\ & + \{\beta_{20} + \beta_{21}[Y]\}[X]^2 + \{\beta_{30}\}[X]^3 \end{aligned}$$

or

$$F_{00}(X, Y) = A + B[X] + C[X]^2 + D[X]^3$$

The original graphical method may be applied to F_{00} if the activity of one of the ligands is held constant while that of the other is varied. The intercept on the F_0 axis in the plot of F_{00} *vs.* [X] gives A, and

$$F_{10} = \frac{F_{00} - A}{[X]} = B + C[X] + D[X]^2$$

By a similar plotting of F_{10} *vs.* [X], B is obtained, and then C and D by iteration.

From the knowledge of C, the mixed stability constant β_{21} may be calculated. In order to determine β_{11} and β_{12}, B must be evaluated at two concentrations of Y.

EXPERIMENTAL

All reagents were of analytical-reagent grade. Potassium oxalate and malonate at pH 7·0 were used as complexing agents. Potassium nitrate was the supporting electrolyte, used to keep the ionic strength constant at 2·1. A 0·004% gelatin solution was used to suppress maxima. All solutions were made up in conductivity water. The experimental technique was the same as described earlier.[5]

RESULTS AND DISCUSSION

Cd–oxalate system

The stability constants were determined by the DeFord and Hume method at pH 7·0 and 27 ± 1°. They were $\log\beta_1 = 2{\cdot}90$, $\log\beta_2 = 4{\cdot}00$, $\log\beta_3 = 5{\cdot}08$, which agree well with those obtained by Schaap and McMasters,[1] considering the difference in ionic strengths used.

Cd–malonate system

Under the same conditions the stability constants were found to be $\log\beta_1 = 1{\cdot}63$, $\log\beta_2 = 2{\cdot}36$, $\log\beta_3 = 3{\cdot}40$ which agree well with those obtained earlier.[3]

The mixed Cd–malonate–oxalate system

The concentration of oxalate was varied while that of the malonate was kept constant, two different values of [Mal] being used, intentionally chosen so that the simple Cd–malonate complex would contain predominantly one or two malonate ions.

Solutions containing $6 \times 10^{-4}M$ Cd^{2+}, $0{\cdot}1524M$ Mal^{2-} and enough potassium nitrate to make $\mu = 2{\cdot}1$ at pH 7·0 and 27°, were polarographed at various oxalate concentrations. In each case a single well-defined diffusion-controlled wave was obtained. The plots of E *vs.* log $i/(i_d - i)$ were linear with slope of 32 ± 1 mV, showing that the two-electron reduction is reversible. The half-wave potentials became more negative with increase in oxalate concentration, indicating mixed complex formation. The experiment was repeated with a malonate concentration of $0{\cdot}2286M$.

The plots of $E_{1/2}$ *vs.* log C_X may be interpreted as three straight lines, showing successive addition of oxalate ions, one in the oxalate concentration range $0{\cdot}00$–$0{\cdot}14M$, the second in the concentration range $0{\cdot}14$–$0{\cdot}28M$ and the third at concentrations $>0{\cdot}28M$.

The constants A, B, C and D were evaluated as described above, and from C, log β_{21} of the complex $Cd(Ox)_2(Mal)$ was found to be 4·96.

From the value of B at the two malonate concentrations log β_{11} and log β_{12} for complexes Cd(Ox)(Mal) and $Cd(Ox)(Mal)_2$ respectively were evaluated as 3·85 and 3·56.

Log β_{21} was also calculated from the second value of C and was found to be 5·02 in good agreement with the first.

Both values of log D (5·12, 5·10) agree with that of log β_2 (5·07) for the simple Cd–oxalate complex.

Acknowledgement—Thanks are due to Prof. R. C. Mehrotra, Head of Department, for providing necessary laboratory facilities. One of the authors (S. C. K.) is thankful to the C.S.I.R. for the grant of a fellowship.

S. C. Khurana
C. M. Gupta

Chemical Laboratories
University of Rajasthan
Jaipur-4, India

Summary—The composition and stability constants of mixed malonate oxalate complexes of cadmium have been determined polarographically. The logarithms of the stability constants of complexes $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal), and $Cd(Ox)_2(Mal)$ were found to be 3·57, 3·86 ± 0·05 and 4·99 ± 0·10 respectively.

Zusammenfassung—Die Zusammensetzung und die Stabilitätskonstanten gemischter Malonat–Oxalat-Komplexe von Cadmium wurden polarographisch bestimmt. Die Logarithmen der Stabilitätskonstanten der Komplexe $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal) und $Cd(Ox)_2(Mal)$ betragen 3,57, 3,86 ± 0,05 bzw. 4,99 ± 0,10.

Résumé—On a déterminé polarographiquement la composition et les constantes de stabilité de complexes mixtes malonate—oxalate du cadmium. On a trouvé que les logarithmes des constantes de stabilité des complexes $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal), et $Cd(Ox)_2(Mal)$ sont respectivement de 3,57; 3,86 ± 0,05 et 4,99 ± 0,10.

REFERENCES

1. W. B. Schaap and D. L. McMaster, *J. Am. Chem. Soc.*, 1961, **83**, 4699.
2. D. D. DeFord and D. N. Hume, *ibid.*, 1951, **73**, 5321.
3. J. K. Gupta, *Ph.D. Thesis*, Rajasthan University, Jaipur, India, 1969.
4. I. Leden, *Z. Physik. Chem. Leipzig*, 1941, **188A**, 160.
5. J. K. Gupta and C. M. Gupta, *Talanta*, 1968, **14**, 274.

Talanta, 1972, Vol. 19, pp. 1236 to 1240. Pergamon Press. Printed in Northern Ireland

Formation of nickel, cobalt, manganese and cadmium ferrocyanides

(*Received* 23 *November* 1971. *Accepted* 27 *December* 1971)

A SYSTEMATIC STUDY has been made of hexacyanoferrates(II), in order to verify the relationship between the properties of the metal ion acting as precipitating agent (ionic dimensions, charge, *etc*)

The mixed Cd–malonate–oxalate system

The concentration of oxalate was varied while that of the malonate was kept constant, two different values of [Mal] being used, intentionally chosen so that the simple Cd–malonate complex would contain predominantly one or two malonate ions.

Solutions containing $6 \times 10^{-4}M$ Cd^{2+}, $0{\cdot}1524M$ Mal^{2-} and enough potassium nitrate to make $\mu = 2{\cdot}1$ at pH 7·0 and 27°, were polarographed at various oxalate concentrations. In each case a single well-defined diffusion-controlled wave was obtained. The plots of E *vs.* log $i/(i_d - i)$ were linear with slope of 32 ± 1 mV, showing that the two-electron reduction is reversible. The half-wave potentials became more negative with increase in oxalate concentration, indicating mixed complex formation. The experiment was repeated with a malonate concentration of $0{\cdot}2286M$.

The plots of $E_{1/2}$ *vs.* log C_X may be interpreted as three straight lines, showing successive addition of oxalate ions, one in the oxalate concentration range $0{\cdot}00$–$0{\cdot}14M$, the second in the concentration range $0{\cdot}14$–$0{\cdot}28M$ and the third at concentrations $>0{\cdot}28M$.

The constants A, B, C and D were evaluated as described above, and from C, log β_{21} of the complex $Cd(Ox)_2(Mal)$ was found to be 4·96.

From the value of B at the two malonate concentrations log β_{11} and log β_{12} for complexes Cd(Ox)(Mal) and $Cd(Ox)(Mal)_2$ respectively were evaluated as 3·85 and 3·56.

Log β_{21} was also calculated from the second value of C and was found to be 5·02 in good agreement with the first.

Both values of log D (5·12, 5·10) agree with that of log β_2 (5·07) for the simple Cd–oxalate complex.

Acknowledgement—Thanks are due to Prof. R. C. Mehrotra, Head of Department, for providing necessary laboratory facilities. One of the authors (S. C. K.) is thankful to the C.S.I.R. for the grant of a fellowship.

S. C. Khurana
C. M. Gupta

Chemical Laboratories
University of Rajasthan
Jaipur-4, India

Summary—The composition and stability constants of mixed malonate oxalate complexes of cadmium have been determined polarographically. The logarithms of the stability constants of complexes $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal), and $Cd(Ox)_2(Mal)$ were found to be 3·57, 3·86 ± 0·05 and 4·99 ± 0·10 respectively.

Zusammenfassung—Die Zusammensetzung und die Stabilitätskonstanten gemischter Malonat–Oxalat-Komplexe von Cadmium wurden polarographisch bestimmt. Die Logarithmen der Stabilitätskonstanten der Komplexe $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal) und $Cd(Ox)_2(Mal)$ betragen 3,57, 3,86 ± 0,05 bzw. 4,99 ± 0,10.

Résumé—On a déterminé polarographiquement la composition et les constantes de stabilité de complexes mixtes malonate—oxalate du cadmium. On a trouvé que les logarithmes des constantes de stabilité des complexes $Cd(Ox)(Mal)_2$, Cd(Ox)(Mal), et $Cd(Ox)_2(Mal)$ sont respectivement de 3,57; 3,86 ± 0,05 et 4,99 ± 0,10.

REFERENCES

1. W. B. Schaap and D. L. McMaster, *J. Am. Chem. Soc.*, 1961, **83**, 4699.
2. D. D. DeFord and D. N. Hume, *ibid.*, 1951, **73**, 5321.
3. J. K. Gupta, *Ph.D. Thesis*, Rajasthan University, Jaipur, India, 1969.
4. I. Leden, *Z. Physik. Chem. Leipzig*, 1941, **188A**, 160.
5. J. K. Gupta and C. M. Gupta, *Talanta*, 1968, **14**, 274.

Talanta, 1972, Vol. 19, pp. 1236 to 1240. Pergamon Press. Printed in Northern Ireland

Formation of nickel, cobalt, manganese and cadmium ferrocyanides

(*Received* 23 *November* 1971. *Accepted* 27 *December* 1971)

A systematic study has been made of hexacyanoferrates(II), in order to verify the relationship between the properties of the metal ion acting as precipitating agent (ionic dimensions, charge, *etc*) and the nature of the compounds formed on interaction with potassium ferrocyanide.[1,2] The interest arises because of the variety of stoichiometric behaviour which can been achieved by the reacting system, in dependence upon the actual reaction conditions.

The anion $Fe(CN)_6^{4-}$ forms a number of compounds with a variety of metals.[3] These species have specific colours, low solubility in water and sometimes a marked tendency to produce colloids. As a consequence ferrocyanide is often used in the identification of some cationic species[4] as well as in the enrichment of trace elements.[5,6] Some authors propose using this reagent quantitatively [7–10] but non-reproducible results are easily obtained because of the variety of factors involved in the reaction with a metal ion.[1,2] It is therefore necessary to know the nature of the products formed under the various experimental conditions.

The types of ferrocyanides formed in solution depend largely on the concentrations of the reagents; the existence of both "normal" and "mixed" ferrocyanides (the latter contain a univalent cation such as K^+, Rb^+, Cs^+, Tl^+, NH_4^+ in constant ratio to the other cation) is known from the literature.[1,2–14]

A systematic investigation[1] of the reaction of ferrocyanide with Cu^{2+}, Zn^{2+}, Pb^{2+} and Ag^+ has established the experimental conditions for formation of $M_2Fe(CN)_6$ and $K_2M_3[Fe(CN)_6]_2$ for Cu, Zn and Pb and of $Ag_4Fe(CN)_6$ and $KAg_3Fe(CN)_6$. The theory has also been given.

The present investigation studies similarly the systems formed by $K_4Fe(CN)_6$ with Ni^{2+}, Co^{2+}, Mn^{2+} and Cd^{2+}, which are known to form various ferrocyanides.[10,11,12–17]

EXPERIMENTAL

Procedure

The potentiometric methods described earlier[1] were used, and the precipitates were analysed for metal content by atomic-absorption spectrophotometry. The cation reagent solutions were standardized by EDTA titration (manganese was also checked spectrophotometrically as permanganate). The potassium ferrocyanide solution was standardized potentiometrically with zinc.

RESULTS

Results for the complexes are summarized in Table I. Table II gives results for the stoichiometry of the reactions and indicates the analytical possibilities.

TABLE I.—COMPLEXES FOUND IN THE REACTION BETWEEN $K_4Fe(CN)_6$ and Ni(II), Co(II), Mn(II) AND Cd(II).

System	Titrand	Formula	pM	in 0·5*M* K^+ medium
Ni(II)	Ni(II)	$K_2Ni_3[Fe(CN)_6]_2$ $K_4Ni_4[Fe(CN)_6]_3$	4·9–3·6 3·2–1·6	$K_4Ni_4[Fe(CN)_6]_3$
	$Fe(CN)_6^{4-}$	$K_2Ni_3[Fe(CN)_6]_2$ $K_4Ni_4[Fe(CN)_6]_3$ $K_{12}Ni_8[Fe(CN)_6]_7$	4·3–3·9 3·4–2·8 2·3–1·6	$K_{12}Ni_8[Fe(CN)_6]_7$
Co(II)	Co(II)	$K_2Co_3[Fe(CN)_6]_2$ $K_4Co_4[Fe(CN)_6]_3$	4·4–2·4 1·9–1·5	$K_{12}Co_8[Fe(CN)_6]_7$
	$Fe(CN)_6^{4-}$	$K_2Co_3[Fe(CN)_6]_2$ $K_4Co_4[Fe(CN)_6]_3$ $K_2Co\ Fe(CN)_6$	4·4–3·4 3·1–2·6 2·3–1·6	$K_2\ Co\ Fe(CN)_6$
Mn(II)	Mn(II)	$K_2Mn_3[Fe(CN)_6]_2$ $K_8Mn_6[Fe(CN)_6]_5$	3·6–2·8 2·4	$K_8Mn_6[Fe(CN)_6]_5$
	$Fe(CN)_6^{4-}$	$K_8Mn_6[Fe(CN)_6]_5$	3·1	$K_8Mn_6[Fe(CN)_6]_5$
Cd(II)*	Cd(II)	$Cd_2Fe(CN)_6$ $K_{12}Cd_8[Fe(CN)_6]_7$†	3·5–1·4 3·0–1·4	$K_{12}Cd_8[Fe(CN)_6]_7$
	$Fe(CN)_6^{4-}$	$K_{12}Cd_8[Fe(CN)_6]_7$	4·3–1·6	$K_{12}Cd_8[Fe(CN)_6]_7$

* Studied at 70° because of slow equilibration of potentials at low temperature.
† Formed in two steps, $Cd_2Fe(CN)_6$ being formed first.

TABLE II.—STOICHIOMETRY OF THE REACTION BETWEEN $K_4Fe(CN)_6$ AND Ni(II), Co(II), Mn(II) AND Cd(II)

Titrand* *μmole*	Titrant *μmole*	Molar ratio $[M]/[Fe(CN)_6^{4-}]$	Formula	Found *μmole*	Error %
Ni(II)	$Fe(CN)_6^{4-}$				
50	32·7	3:2	$K_2Ni_3[Fe(CN)_6]_2$	49	−2
100	66·8	3:2	$K_2Ni_3[Fe(CN)_6]_2$	100·2	+0·2
$Fe(CN)_6^{4-}$	Ni(II)				
25	37·5	3:2	$K_2Ni_3[Fe(CN)_6]_2$	25·0	0
175	232	4:3	$K_4Ni_4[Fe(CN)_6]_3$	174	−0·6
200	264.6	4:3	$K_4Ni_4[Fe(CN)_6]_3$	198·4	−0·8
Co(II)	$Fe(CN)_6^{4-}$				
150	99·7	3:2	$K_2Co_3[Fe(CN)_6]_2$	149·6	−0·3
250	169	3:2	$K_2Co_3[Fe(CN)_6]_2$	253·5	+1·4
$Fe(CN)_6^{4-}$	Co(II)				
12·5	18·8	3:2	$K_2Co_3[Fe(CN)_6]_2$	12·53	+0·2
75	99·1	4:3	$K_4Co_4[Fe(CN)_6]_3$	74·3	−0·9
122	163	4:3	$K_4Co_4[Fe(CN)_6]_3$	122·3	+0·2
Mn(II)	$Fe(CN)_6^{4-}$				
99	65	3:2	$K_2Mn_3[Fe(CN)_6]_2$	97·5	−1·8
147	99	3:2	$K_2Mn_3[Fe(CN)_6]_2$	148·5	+1·0
742	612·5	6:5	$K_8Mn_6[Fe(CN)_6]_5$	735	−0·9
$Fe(CN)_6^{4-}$	Mn(II)				
500	616·2	6:5	$K_8Mn_6[Fe(CN)_6]_5$	513	+2·6
750	894	6:5	$K_8Mn_6[Fe(CN)_6]_5$	745	−0·7
Cd(II)	$Fe(CN)_6^{4-}$				
15·4	13·34	8:7	$K_{12}Cd_8[Fe(CN)_6]_7$	15·2	−1·3
231	202	8:7	$K_{12}Cd_8[Fe(CN)_6]_7$	230·9	0
$Fe(CN)_6^{4-}$	Cd(II)				
26·1	29·3	8:7	$K_{12}Cd_8[Fe(CN)_6]_7$	25·6	−1·9
522	598·3	8:7	$K_{12}Cd_8[Fe(CN)_6]_7$	523·5	+0·3

* In 100 ml of solution.

Solubility products and thermodynamic formation functions

K_{sp} values were obtained by conductivity measurements on saturated solutions free from oxygen and carbon dioxide, except for $K_{12}Co_8[Fe(CN)_6]_7$ and $K_2CoFe(CN)_6$ (because of their easy alteration). Equivalent limiting conductivities at 20 and 25° were obtained from literature data; values at 30°, 35° and 45° were obtained by Walden's rule.[18]

Enthalpies for the Ni(II) and Co(II) complexes were calculated from

$$\Delta H = -T^2\left[\frac{\partial(\Delta G/T)}{\partial T}\right],$$

assuming that the incremental ratio $\left[\frac{\Delta(\Delta G/T)}{\Delta T}\right]$, between 20 and 30° may be identified with $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]$, at 25°.

For the Mn(II) and Cd(II) complexes, for which the K_{sp} values are available at three temperatures, the following relationships were obtained by the least-squares method:[19]

$$\Delta G_T = -40{\cdot}28 - 2{\cdot}49 \times 10^{-1}\,(\Delta T) + 5{\cdot}7 \times 10^{-3}\,(\Delta T)^2 \text{ for } K_2Mn_3[Fe(CN)_6]_2$$
$$\Delta G_T = -88{\cdot}08 - 0{\cdot}086\,(\Delta T) - 6{\cdot}0 \times 10^{-3}\,(\Delta T)^2 \text{ for } K_8Mn_6[Fe(CN)_6]_5$$
$$\Delta G_T = -18{\cdot}34 + 0{\cdot}165\,(\Delta T) - 7{\cdot}3 \times 10^{-3}\,(\Delta T)^2 \text{ for } Cd_2Fe(CN)_6$$
$$\Delta G_T = -165{\cdot}1 + 3 \times 10^{-2}\,(\Delta T) \text{ for } K_{12}Cd_8[Fe(CN)_6]_7$$

Though the use of temperature coefficients is sometime advised[20] for evaluating heats and entropies of formation from the logarithm of the stability constants, in this case we have obtained an unlikely dependence of ΔH on temperature for the complexes $K_2Mn_3[Fe(CN)_6]_2$, $K_8Mn_6[Fe(CN)_6]_5$ and $Cd_2Fe(CN)_6$. This may be due to a limited validity of the expressions derived from only three points or the large multiplication of experimental error arising from the complexity of the compounds. We think that the best values for obtaining ΔH and ΔS are those at 35°, first because they are the ones least affected by limiting conditions and secondly because they are in agreement with the values obtained by two other methods. The results show that the $-\Delta H$ sequence of $d^6 < d^7 < d^8$ expected for stabilization due to the ligand field[20,21] is observed for every value of ΔH for $K_2M_3[Fe(CN)_6]_2$ obtained from the equations written above.

The results are summarized in Table III.

TABLE III.—K_{sp}, ΔG^0, ΔH^0 AND ΔS^0 VALUES

Formula	Temp. °C	Solubility, *M*	K_{sp}	ΔG^0, *kcal/mole*	ΔH^0, *kcal/mole*	ΔS^0, *kcal/mole*$^{-1}$ K^{-1}
$K_2Ni_3[Fe(CN)_6]_2$	20	$6{\cdot}70 \times 10^{-6}$	$2{\cdot}6 \times 10^{-34}$	$-45{\cdot}1$	$-99{\cdot}8$	$-0{\cdot}19$
	30	$1{\cdot}45 \times 10^{-5}$	$5{\cdot}0 \times 10^{-32}$	$-43{\cdot}2$		
$K_4Ni_4[Fe(CN)_6]_3$	20	$1{\cdot}31 \times 10^{-5}$	$3{\cdot}5 \times 10^{-48}$	$-63{\cdot}4$	—	—
$K_{12}Ni_8[Fe(CN)_6]_7$	20	$6{\cdot}70 \times 10^{-6}$	$2{\cdot}5 \times 10^{-114}$	-152	—	—
$K_2Co_3[Fe(CN)_6]_2$	20	$4{\cdot}46 \times 10^{-5}$	$1{\cdot}5 \times 10^{-28}$	$-37{\cdot}3$	$-77{\cdot}6$	$-0{\cdot}137$
	30	$6{\cdot}05 \times 10^{-5}$	$1{\cdot}3 \times 10^{-27}$	$-35{\cdot}9$		
$K_4Co_4[Fe(CN)_6]_3$	20	$1{\cdot}88 \times 10^{-5}$	$1{\cdot}9 \times 10^{-46}$	$-61{\cdot}3$	$-84{\cdot}7$	$-0{\cdot}08$
	30	$2{\cdot}83 \times 10^{-5}$	$1{\cdot}7 \times 10^{-44}$	$-60{\cdot}5$		
$K_2Mn_3[Fe(CN)_6]_2$	25	$2{\cdot}54 \times 10^{-5}$	$2{\cdot}9 \times 10^{-30}$	$-40{\cdot}3$	$-0{\cdot}62$	$+0{\cdot}135$
	35	$2{\cdot}21 \times 10^{-5}$	$1{\cdot}1 \times 10^{-30}$	$-42{\cdot}2$		
	45	$2{\cdot}54 \times 10^{-5}$	$2{\cdot}9 \times 10^{-30}$	-43		
$K_6Mn_6[Fe(CN)_6]_5$	25	$6{\cdot}18 \times 10^{-5}$	$2{\cdot}6 \times 10^{-65}$	$-88{\cdot}1$	$-26{\cdot}1$	$+0{\cdot}206$
	35	$7{\cdot}0 \times 10^{-5}$	$2{\cdot}8 \times 10^{-64}$	$-89{\cdot}5$		
	45	$7{\cdot}20 \times 10^{-5}$	$4{\cdot}7 \times 10^{-64}$	$-92{\cdot}2$		
$Cd_2Fe(CN)_6$	25	$2{\cdot}07 \times 10^{-5}$	$3{\cdot}6 \times 10^{-14}$	$-18{\cdot}3$	-23	$+0{\cdot}019$
	35	$4{\cdot}76 \times 10^{-5}$	$4{\cdot}3 \times 10^{-13}$	$-17{\cdot}4$		
	45	$4{\cdot}82 \times 10^{-5}$	$4{\cdot}5 \times 10^{-8}$	-18		
$K_{12}Cd_8[Fe(CN)_6]_7$	25	$3{\cdot}50 \times 10^{-6}$	$8{\cdot}9 \times 10^{-122}$	-165	-173	$-0{\cdot}03$
	35	$6{\cdot}10 \times 10^{-6}$	$2{\cdot}4 \times 10^{-117}$	-164		
	45	6.90×10^{-6}	$5{\cdot}3 \times 10^{-114}$	-165		

Conclusions

The stability (ΔG°) of these ferrocyanides in the sequence Zn > Cu > Ni > Mn ~ Co leads to the disappearance of simple forms such as $M_2Fe(CN)_6$, mixed species containing some K^+ appearing. The complex $K_2M_3[Fe(CN)_6]_2$ has probably some peculiarly stable structural properties, since its existence has been found in all the systems investigated.

Acknowledgement—This work was partially supported by the Consiglio Nazionale delle Ricerche and was presented at the C.N.R. meeting "Metodologie Analitiche, equilibri in soluzione e termodinamica chimica," Rome (Italy). 1–3 December 1969.

Institute of Analytical Chemistry
University of Messina
Messina, Italy

ATHOS BELLOMO
DOMENICO DE MARCO
AGATINO CASALE

Summary—Potentiometric and solubility studies have been made of the ferrocyanides of nickel, cobalt, manganese(II) and cadmium both in the presence and absence of potassium. The K_{sp}, ΔG°, ΔH° and ΔS° values are reported.

Zusammenfassung—Es wurden potentiometrische und Löslbarkeitsuntersuchungen an Cyaneisenverbindungen von Zink, Kuppfer(II), Nickel, Mangan II und Kobalt II sowohl mit und ohne Vorhandensein von Kalium vorgenommen. Es werden die K_{sp}, ΔG°, ΔH° und ΔS° Werte angegeben.

Résumé—On a effectué des études potentiométrique et de solubilité des ferrocyanures de nickel, cobalt, manganèse(II) et cadmium toutes deux en la présence et l'absence de potassium. On rapporte les valeurs de K_{sp}, $\Delta G°$, $\Delta H°$ et $\Delta S°$.

REFERENCES

1. A. Bellomo, *Talanta*, 1970, **17**, 1109.
2. A. Bellomo, D. De Marco and A. Casale, Proc. 2nd Conf. *Appl. Phy. Chem. 4th Symp. Oscillometry*, Veszprem, Hungary, 1971.
3. K. L. Cheng, *Anal. Chem.*, 1955, **23**, 1594,.
4. G. Jander and H. Wendt, *Lehrbuch der analytischen und präparativen anorganischen Chemie*, Hirzel Verlag, Stuttgart, 1959.
5. W. Prandtl, *Z. Anorg. Allgem. Chem.* 1932, **208**, 420.
6. I. V. Tananaev and M. A. Cluskova, *Zh. Prikl. Khim.*, 1959, **32**, 1899.
7. I. M. Koltoff and A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, 1945, 4, 171.
8. E. L. Nimer, R. E. Hamm and G. L. Lee, *Anal. Chem.* 1950, **22**, 970.
9. D. F. Swinehart, *ibid.*, 1951, **23**, 381.
10. J. S. Beshmukh and M. Venucopalan, *J. Indian Chem. Soc.*, 1957, **33**, 222.
11. I. V. Tananaev and M. I. Levina, *Zh. Analit. Khim.* 1946, **1**, 224.
12. F. N. Deichman and I. V. Tananaev, *Khim. Redkikh Elementov, Akad. Nauk SSSR Inst.Obshch. i Neorgan. Khim.*, 1955, **2**, 37.
13. I. V. Tananaev and M. I. Levina, *Zh. Analit. Khim.*, 1947, **3**, 31.
14. W. U. Malik and A. K. Bhattacharya, *Agra Univ. J. Research.* 1957, **1**, 25.
15. I. V. Tananaev and A. P. Korolkov, *Isv. Akad. Nauk. SSSR Neorgan. Materialy*, 1955, **1**, 607.
16. A. K. Bhattacharya and H. C. Gaur, *J. Indian Chem. Soc.*, 1948, **25**, 185.
17. *Idem*, *ibid.*, 1948, **25**, 220.
18. H. S. Harned and B. D. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1964.
19. G. Barbensi, *Elementi di matematica generale*, Casa Editrice Macri, Firenze, 1945.
20. F. J. C. Rossotti, in *Modern Coordination Chemistry*, edited J. Lewis and R. G. Wilkins, Interscience, New York, 1960.
21. L. E. Orgel, *Introduzione alla chimica dei metalli di transizione*, Feltrinelli editore, Milano, 1963.

Talanta, 1972, Vol. 19, pp. 1240 to 1243. Pergamon Press. Printed in Northern Ireland

The acid dissociation constants of 2,3-quinoxalinedithiol

(*Received* 20 *January* 1972. *Accepted* 20 *February* 1972)

SINCE the preparation of 2,3-quinoxalinedithiol (H_2qdt) by Morrison and Furst in 1956,[1] many publications on its use as an analytical reagent have appeared.[2] Information on the properties of the reagent itself is scarce, however, and as yet there are no published data on the ionization constants. Stevančević and Dražić[3] attempted to obtain these constants by a spectrophotometric method but concluded erroneously that they were too close to be determined by such methods.

In order to rationalize the analytical procedures and to predict the optimum working conditions, the ionization constants of H_2qdt have been determined by potentiometric titration and solubility measurements.

EXPERIMENTAL

Reagents

2,3-*Quinoxalinedithiol.* Prepared as described previously[4] and purified by dissolving the crude product in sodium hydroxide, under a nitrogen atmosphere, reprecipitating it with acetic acid, and repeating the process. The product was dried at 100° under vacuum. Elemental analysis of the purified material gave C, 49·7%; H, 3·3%; N, 14·2%; S, 32·3% $C_8H_6N_2S_2$ requires C, 49·5%; H, 3·1%; N, 14·4%; S, 33·0%.

Sodium salts. Prepared by mixing H_2qdt with the calculated volume of 4*M* sodium hydroxide and evaporating under reduced pressure. The crude product was purified by dissolving it in the minimum volume of aqueous ethanol, filtering, and adding a large excess of diethyl ether. The bright yellow-orange material was filtered off, washed with ether and dried under vacuum. Elemental analysis of the

Résumé—On a effectué des études potentiométrique et de solubilité des ferrocyanures de nickel, cobalt, manganèse(II) et cadmium toutes deux en la présence et l'absence de potassium. On rapporte les valeurs de K_{sp}, $\Delta G°$, $\Delta H°$ et $\Delta S°$.

REFERENCES

1. A. Bellomo, *Talanta*, 1970, **17**, 1109.
2. A. Bellomo, D. De Marco and A. Casale, Proc. 2nd Conf. *Appl. Phy. Chem. 4th Symp. Oscillometry*, Veszprem, Hungary, 1971.
3. K. L. Cheng, *Anal. Chem.*, 1955, **23**, 1594,.
4. G. Jander and H. Wendt, *Lehrbuch der analytischen und präparativen anorganischen Chemie*, Hirzel Verlag, Stuttgart, 1959.
5. W. Prandtl, *Z. Anorg. Allgem. Chem.* 1932, **208**, 420.
6. I. V. Tananaev and M. A. Cluskova, *Zh. Prikl. Khim.*, 1959, **32**, 1899.
7. I. M. Koltoff and A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, 1945, 4, 171.
8. E. L. Nimer, R. E. Hamm and G. L. Lee, *Anal. Chem.* 1950, **22**, 970.
9. D. F. Swinehart, *ibid.*, 1951, **23**, 381.
10. J. S. Beshmukh and M. Venucopalan, *J. Indian Chem. Soc.*, 1957, **33**, 222.
11. I. V. Tananaev and M. I. Levina, *Zh. Analit. Khim.* 1946, **1**, 224.
12. F. N. Deichman and I. V. Tananaev, *Khim. Redkikh Elementov, Akad. Nauk SSSR Inst.Obshch. i Neorgan. Khim.*, 1955, **2**, 37.
13. I. V. Tananaev and M. I. Levina, *Zh. Analit. Khim.*, 1947, **3**, 31.
14. W. U. Malik and A. K. Bhattacharya, *Agra Univ. J. Research.* 1957, **1**, 25.
15. I. V. Tananaev and A. P. Korolkov, *Isv. Akad. Nauk. SSSR Neorgan. Materialy*, 1955, **1**, 607.
16. A. K. Bhattacharya and H. C. Gaur, *J. Indian Chem. Soc.*, 1948, **25**, 185.
17. *Idem*, *ibid.*, 1948, **25**, 220.
18. H. S. Harned and B. D. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1964.
19. G. Barbensi, *Elementi di matematica generale*, Casa Editrice Macri, Firenze, 1945.
20. F. J. C. Rossotti, in *Modern Coordination Chemistry*, edited J. Lewis and R. G. Wilkins, Interscience, New York, 1960.
21. L. E. Orgel, *Introduzione alla chimica dei metalli di transizione*, Feltrinelli editore, Milano, 1963.

Talanta, 1972, Vol. 19, pp. 1240 to 1243. Pergamon Press. Printed in Northern Ireland

The acid dissociation constants of 2,3-quinoxalinedithiol

(*Received* 20 *January* 1972. *Accepted* 20 *February* 1972)

SINCE the preparation of 2,3-quinoxalinedithiol (H_2qdt) by Morrison and Furst in 1956,[1] many publications on its use as an analytical reagent have appeared.[2] Information on the properties of the reagent itself is scarce, however, and as yet there are no published data on the ionization constants. Stevančević and Dražić[3] attempted to obtain these constants by a spectrophotometric method but concluded erroneously that they were too close to be determined by such methods.

In order to rationalize the analytical procedures and to predict the optimum working conditions, the ionization constants of H_2qdt have been determined by potentiometric titration and solubility measurements.

EXPERIMENTAL

Reagents

2,3-*Quinoxalinedithiol.* Prepared as described previously[4] and purified by dissolving the crude product in sodium hydroxide, under a nitrogen atmosphere, reprecipitating it with acetic acid, and repeating the process. The product was dried at 100° under vacuum. Elemental analysis of the purified material gave C, 49·7%; H, 3·3%; N, 14·2%; S, 32·3% $C_8H_6N_2S_2$ requires C, 49·5%; H, 3·1%; N, 14·4%; S, 33·0%.

Sodium salts. Prepared by mixing H_2qdt with the calculated volume of 4*M* sodium hydroxide and evaporating under reduced pressure. The crude product was purified by dissolving it in the minimum volume of aqueous ethanol, filtering, and adding a large excess of diethyl ether. The bright yellow-orange material was filtered off, washed with ether and dried under vacuum. Elemental analysis of the disodium salt (dihydrate) gave C, 35·2%; H, 3·1%; N, 10·1%; S, 23·3%; Na, 16·8%. $C_8H_8N_2S_2O_2$-Na_2 requires C, 35·0; H, 2·9%; N, 10·2%; S, 23·4%; Na, 16·8%.

Perchloric acid. Prepared by dilution of the analytical grade acid and standardized with sodium carbonate.

Buffer solutions. For the pH range 3·0–10·5 buffer solutions recommended by Albert and Serjeant[5] were used, and Walpole buffers[6] for the pH range 0·7–3·0.

Procedure

Sodium salts of H_2qdt (100-ml portions of 0·001–0.01*M* solutions) were titrated potentiometrically at 20° under a nitrogen atmosphere with perchloric acid. The titrations were repeated at 25° and at ionic strength 0.1 (added sodium perchlorate) but no significant differences were observed.

Solubility measurements were carried out by preparing saturated solutions of H_2qdt in 0·1*M* sodium chloride and 0·005*M* buffer, equilibrating them by shaking for 3 hr at constant temperature, filtering, measuring the pH of the filtrate and determining the H_2qdt in the filtrate absorptiometrically as the $[Zn(qdt)_2]^{2-}$ complex, at pH 10 and 390 nm.

RESULTS AND DISCUSSION

The sodium salts are much more soluble than H_2qdt in water, *e.g.*, up to 2*M* solutions of the disodium salt can be prepared, and $Na_2qdt.2H_2O$ provides an excellent form of the analytical reagent because of its relative stability. Potentiometric titration of 0·01*M* Na_2qdt with perchloric acid clearly indicates the dibasic character of the reagent (see Fig. 1).

The region of the titration curve corresponding to addition of up to one equivalent of acid was used directly to obtain pK_2 by the method of Albert and Serjeant.[5] Typical results are shown in Table I. The mean value and spread found at 20° were 9·95 ± 0·03.

pK_1 could not be obtained directly because H_2qdt precipitated on addition of more than one equivalent of acid. For this region of the titration curve the method of Dyrssen and Hoek,[7] as described by King,[8] was therefore used. By applying the condition of electroneutrality to points on the curve corresponding to a saturated solution of H_2qdt (see Fig. 1), a series of values for the solubility product $K_s = [H^+][Hqdt^-]$ was obtained. Typical results are shown in Table II. The mean value

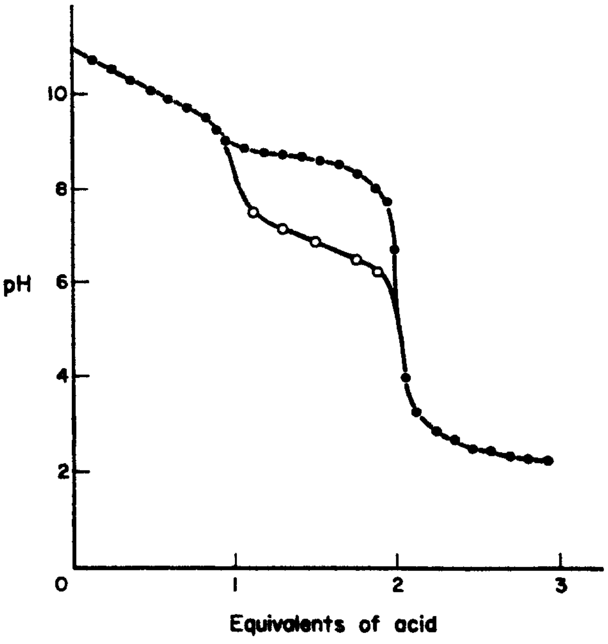


FIG. 1.—Potentiometric titration of 0·01*M* 2.3-quinoxalinedithiol (disodium salt) with 0·482*M* perchloric acid (20°).

● Experimental points

○ Points calculated for $pK_1 = 6·84$

(precipitation of H_2qdt occurred from pH 8·9 downwards).

TABLE I.—DETERMINATION OF pK_2 OF 2,3-QUINOXALINEDITHIOL FROM POTENTIOMETRIC TITRATION OF ITS DISODIUM SALT AT 0·01M CONCENTRATION AND 20° (TRITRANT: 0·482M PERCHLORIC ACID)

Titrant, *ml*	pH	qdt^{2-} present, *mmole*	$\log\left(\frac{[Hqdt^-] + a_{OH^-}}{[qdt^{2-}] - a_{OH^-}}\right)^*$	pK_2
0	10·93	0·9378		
0·2	10·75	0·8414	−0·79	9·94
0·4	10·50	0·7450	−0·53	9·97
0·6	10·30	0·6486	−0·32	9·98
0·8	10·10	0·5522	−0·14	9·96
1·0	9·90	0·4558	+0·03	9·93
1·2	9·73	0·3594	+0.21	9·94
1·4	9·0	0·2609	+0·42	9·92

* a_{OH^-} = hydroxyl ion activity.

TABLE II.—DETERMINATION OF THE SOLUBILITY PRODUCT (K_s) OF 2,3-QUINOXALINEDITHIOL FROM POTENTIOMETRIC TITRATION OF ITS DISODIUM SALT AT 0·01M CONCENTRATION AND 20° (TITRANT: 0·482M PERCHLORIC ACID)

$Hqdt^-$ titrated, *mmole*	0·1928	0·2892	0·3856	0·4020	0·5784	0·6784
pK_s	10·88	10·89	10·95	10·89	10·94	10·88

and spread found for pK_s at 20° were 10·91 ± 0·04. The solubility of un-ionized H_2qdt (S_0), measured at 20°, was 7·2 × $10^{-5}M$. pK_1 was calculated by using the relationship

$$K_1 = \frac{[H^+][Hqdt^-]}{[H_2qdt]} = \frac{K_s}{S_0}$$

The value found for pK_1 was 6·80 ± 0·04. Similar results were obtained from potentiometric titration of the monosodium salt of H_2qdt.

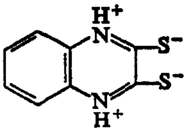
Measurements of solubilities in buffered solutions showed that the solubility of H_2qdt remains constant in the pH range 0·7–5·0 and is equal to S_0. Above pH 5 there is a marked increase in solubility. Solubilities in the pH range 5·0–8·5 were used to obtain pK_1 by the method of Krebs and Speakman,[8] also described by King.[9] The relevant equation is:

$$\log\left(\frac{S}{S_0} - 1\right) = \mathrm{pH} - \mathrm{p}K_1$$

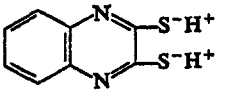
where S is the solubility of H_2qdt at a given pH. The pK_1 value obtained graphically by this method was 6·86 at 20°. Above pH 8·5 H_2qdt becomes extremely soluble and the solubility method cannot be used to determine pK_2.

The average values of the constants found in the present work are pK_1 = 6·84 and pK_2 = 9·95. They must be regarded essentially as the "mixed" acid ionization constants since activity corrections were not applied. However, as the determinations were carried out in solutions not stronger than 0.01M, the values of the thermodynamic constants may not be significantly different. The two pK values are sufficiently far apart to be determined sequentially with good precision.

It can be concluded that H_2qdt behaves as a dibasic acid and is not itself protonated at pH values not below 0·7. Lower pH values were not investigated. It would be of interest to know whether the acid protons are associated with sulphur or nitrogen atoms. The following extreme structures of H_2qdt are possible



(I)



(II)

as well as thiol-thione tautomeric forms.[10] The absence of any basic (proton-acceptor) properties in H_2qdt suggests structure (I) as the most probable. Other work carried out in these laboratories,[10] particularly infrared spectroscopic and preparative evidence, supports this view, which has bearing on the applications of H_2qdt as an analytical reagent.

Acknowledgements—We acknowledge with gratitude the grant of study leave from Kingston Polytechnic to A. K. S.

J. A. W. Dalziel
A. K. Slawinski*

Department of Chemistry
Chelsea College of Science and Technology
Manresa Road, London, S.W.3.

---

* Present address: School of Chemical Science and Technology, Kingston Polytechnic, Kingston-upon-Thames, Surrey, U.K.

Summary—Sodium salts of 2,3-quinoxalinedithiol have been prepared and used for determination of the acid ionization constants by potentiometric titration. The fully protonated form of the reagent was used in an alternative determination of the first ionization constant by a solubility method. The constants are $pK_1 = 6·84 \pm 0·04$ and $pK_2 = 9·95 \pm 0·03$.

Zusammenfassung—Es wurden Natrium Salze von 2,3-Chinoxalindithiol vorbereitet und zur Ermittlung der Säureionisationskonstanten durch potentiometrische Titrierung benutzt. Die völlig protonierte Form des Reagenz wurde mit einem Löslichkeitsverfahren in einer anderen Feststellung der ersten Ionisationskonstante verwandt. Die Konstanten sind $pK_1 = 6,84 \pm 0,04$ und $pK_2 = 9,95 \pm 0,03$.

Résumé—On a préparé les sels de sodium du 2,3-quinoxalinedithiol et les a utilisés pour la détermination des constantes d'ionisation acides par titrage potentiométrique. On a utilisé la forme totalement protonée du réactif dans une autre possibilité de détermination de la constante de première ionisation par une méthode de solubilité. Les constantes sont $pK_1 = 6,84 \pm 0,04$ et $pK_2 = 9,95 \pm 0,03$.

REFERENCES

1. D. M. Morrison and A. J. Furst, *J. Org. Chem.*, 1956, **21**, 470.
2. *e.g.*, R. W. Burke and E. R. Deardorff, *Talanta*, 1970, **17**, 255 and references therein.
3. D. B. Stevančević and V. G. Dražič, *Bull. Inst. Nuclear Sci., Boris Kidrich, Belgrade*, 1959, **9**, 69.
4. J. A. W. Dalziel and A. K. Slawinski, *Talanta*, 1968, **15**, 367.
5. A. Albert and E. P. Serjeant, *Ionization Constants of Acids and Bases*, Methuen, London, 1962.
6. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, 3rd Ed., Longmans, London, 1961.
7. D. Dyrssen and B. Hoek, *Svensk. Kem. Tidskr.*, 1952, **64**, 80.
8. E. J. King, *Acid-Base Equilibria*, Pergamon, Oxford, 1965.
9 H. A. Krebs and J. C. Speakman, *J. Chem. Soc.*, 1945, 593.
10. A. K. Slawinski, *Ph.D. Thesis*, University of London, 1970.

Talanta, 1972, Vol. 19, pp. 1245 to 1283. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

SYNTHETIC INORGANIC ION EXCHANGERS—II

SALTS OF HETEROPOLYACIDS, INSOLUBLE FERROCYANIDES, SYNTHETIC ALUMINOSILICATES AND MISCELLANEOUS EXCHANGERS

V. PEKÁREK† and V. VESELÝ
Nuclear Research Institute of the Czechoslovak Academy of Sciences,
Řež near Prague, Czechoslovakia

(*Received* 18 *June* 1971. *Accepted* 7 *February* 1972)

Summary—A review of the developments during the period 1965–70 in use of heteropoly acid salts, ferrocyanides and synthetic zeolites as ion-exchangers.

IN PART I[1] the ion-exchange properties of hydrous oxides and acidic salts of multivalent metals were described. In this part the progress made during the period 1965–1970 in studying the exchange properties of heteropoly acid salts, insoluble ferrocyanides, synthetic aluminosilicates and certain other substances will be reviewed.

SALTS OF HETEROPOLY ACIDS

The parent acids of the compounds considered in this section are the 12-heteropoly acids of the general formula $H_mXY_{12}O_{40}\cdot nH_2O$ ($m = 3, 4, 5$), where X may be phosphorus, arsenic, silicon, germanium, and boron, and Y different elements such as molybdenum, tungsten, and vanadium. The basic physicochemical and ion-exchange properties of these compounds have been widely described in many earlier papers and surveyed in the book by Amphlett.[2] The emphasis during the last five years has been on the applications of these compounds, especially the 12-molybdophosphates.

Molybdophosphates

12-Molybdophosphates (MP) of the alkali metals and NH_4^+, prepared by metathesis in acid solutions, are salts with base-equivalent ranging from 1·82 to 2·48 per mole. Nearly neutral salts with base-equivalents of 2·9 are prepared by neutralization. The salts of bivalent metals have base-equivalents varying from 2·68 to 3·10. All compounds examined, although non-stoichiometric, are true compounds with the water content generally lower for the alkali metal salts than for the bivalent metal salts and their thermal stability follows the order Rb > Cs > K > Na > Li.[3] Anhydrous salts of MP with pyridinium, lutidinium and collidinium cations have been described. These salts proved worse exchangers than the corresponding tungstophosphates.[4] Tungstophosphates retained $2H_2O$ of crystallization after drying at 150°, whereas MP and tungstosilicates became anhydrous.[5]

Like inorganic tungstophosphates all the MP form normal (X_3MP) and acidic

---

* Part I—*Talanta*, 1972, **19**, 219. For reprints of this Review see Publisher's announcement near end of this issue.

† Present address: Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences, Prague 6, Czechoslovakia.

(X_2HMP) salts, but no diacidic (XH_2MP) salts. The main factor influencing the formation of normal or acid insoluble MP is the original X:Y ratio. The effect of hydrogen ions is of secondary importance, but is more decisive for tungstophosphate formation.[5] The following salts of MP were prepared:[5] Tl_3MP, Tl_2HMP, Cs_3MP, Cs_2HMP, Rb_3MP, Rb_2HMP, $(NH_4)_3MP$, $(NH_4)_2HMP$, K_3MP, K_2HMP, Hg_3MP, and Ag_3MP. The rate of Cs^+ and Rb^+ exchange in Tl_3MP is slower than with the NH_4^+ analogue,[6] and because thallium is bound more firmly than the proton the exchange is between the alkali metal and hydrogen ions. Caesium is adsorbed more easily than rubidium. Highest separation factors for caesium from rubidium were found on Tl_2HMP. The presence of thallium in the solution substantially depressed the caesium adsorption.[6] The preparation and properties of alkali metal salts of MP have been reviewed by Thistlethwaite.[7]

Ammonium molybdophosphate. Ammonium molybdophosphate (AMP) was the first MP salt to be used for practical separations and to be the subject of basic adsorption and physicochemical studies.

The preparation and properties of neutral and acid salts of $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_2HPMo_{12}O_{40}$ have been described in detail by Healy[5] and Krtil.[6] Coarse AMP which allowed adequate flow-rates in large-scale columns without the need of carriers was prepared by Smit[8] by direct conversion of 12-molybdophosphoric acid into the ammonium salts. Rapid, irreversible, exchange of NH_4^+ for H^+ occurs in the solid and the conversion is accompanied by a phase transition. Each particle of the product consists of a stable agglomerate of microcrystals of about 1 μm diameter. The porosity permits a high rate of exchange.[8]

The capacity of AMP for caesium was found to be 1·0 meq/g and corresponds to the formation of Cs_2NH_4MP. Caesium is more easily adsorbed by the normal than the acidic ammonium salts. On the acidic salts caesium is exchanged only for protons at higher acidities.[6] The exchange of caesium for the first equivalent of ammonium ion is easier, than that for the second. Smaller alkali metal cations are exchanged as partially hydrated ions.[9] Coetzee[9] studied the sorption properties of AMP by the column chromatography method. However, the saturation capacities had no direct relation to the stoichiometric exchange of one or two equivalents of NH_4^+. Ammonium ions lowered strongly the sorption of Li^+, Na^+, K^+ and H_3O^+ but only a small effect on the Rb^+, Cs^+ and Tl^+ exchange was observed. The following affinity series was derived: $Cs^+ = Tl^+ > Rb^+ > Ag^+ > K^+ > H_3O^+ > Na^+ > Li^+$. The bonds between Tl^+, Ag^+ and the molybdophosphate anion are supposed to be partially covalent, because the adsorption of Ag^+ and Tl^+ was much higher than that of alkali metal ions of the same size.

The sorption behaviour of UO_2^{2+} on AMP was studied under static conditions as a function of the HNO_3, H_2SO_4, NH_4NO_3 and UO_2^{2+} concentration. The UO_2OH^+ cation was proved to be adsorbed at low acidities.[10] The thorium (IV) adsorption was examined in HNO_3 and H_2SO_4 solutions of various concentrations. Linear log K_d *vs.* log $[H^+]$ plots of different slopes were obtained, depending upon ammonium ion and proton concentration.[11] The Th^{4+}–NH_4^+ exchange is controlled by the law of mass action and the mechanism was proved to be ion-exchange except for the acidity range $<0{\cdot}01M$, where the adsorption process was complicated by hydrolysis. Partial irreversibility of Th^{4+} adsorption and relatively slow adsorption kinetics were ascribed to the probable formation of a Th^{4+}–heteropoly-anion complex.[11]

Practical AMP applications are of great interest. AMP has been applied for the concentration and purification of caesium-137 to give spectrally pure γ-sources[12] and for the determination of caesium in rain water[13] and fast-reactor coolants.[14]

Caesium-137 present in the nuclear reactor coolants was separated from ^{103}Ru on AMP. Ruthenium was only partially retained by this sorbent and therefore the contamination of caesium by ruthenium increased with increasing ruthenium content in the coolant.[15] Separation of Rb^+, Cs^+, K^+, Tl^+ and Ag^+ from acid solutions and from Na^+ or Li^+ has been successfully performed on AMP.[12,16] Rb^+, Tl^+ and Cs^+ were sorbed from 5*M* HNO_3, but Na^+ and K^+ were adsorbed negligibly by the exchanger supported on asbestos. Direct Tl^+–Cs^+ separation at tracer levels by using NH_4NO_3 as eluent was very difficult. Rb^+ was therefore eluted with 3*M* NH_4NO_3, thallium separated by oxidative elution with 0·05*M* Br_2 in 5% HBr and Cs^+ eluted with 12*M* NH_4NO_3.[17] Na^+–K^+–Rb^+–Cs^+ mixtures were completely separated on AMP with well-distinguished peaks, whereas an organic cation-exchanger (Dowex 50) required 250 times the bed depth to achieve such a resolution.[12] Up to 0·1 meq of K^+ can be separated quantitatively from amounts of up to 50 meq of Na^+ on a small column with 4 g of AMP supported by glass wool and an asbestos mat. Na^+ was eluted with 0·01*M* HNO_3 and K^+ with 0·25*M* NH_4NO_3.[18] Astatine was co-precipitated with Cs^+, NH_4^+ and K^+ salts of molybdophosphoric acid after oxidation with $Cr_2O_7^{2-}$ in HNO_3 solutions.[19] Sorption of Cs^+ and Rb^+ on $(NH_4)_3MP$ and $(NH_4)_2HMP$ from aqueous alcohol media was higher than from aqueous solutions, but the separation of these elements was not affected by this organic–aqueous mixture.[6]

Membrane electrodes made from AMP were prepared under a pressure of 150 atm with polystyrene, polyethylene and polymethacrylate as binders. The membrane potentials were measured for two-component systems of NH_4^+, Na^+, K^+, Li^+ and Cs^+ and the dependence on the concentration was found to be linear up to 3*M*.[20]

Tungstophosphates (WP)

The second most widely studied group of heteropolyacids are the tungstophosphates. The following mixed alkali metal salts of $H_3PW_{12}O_{40}$ have been prepared:[21] Cs_2NaWP, Cs_2KWP, Cs_2RbWP, Cs_2LiWP, $(NH_4)_2CsWP$, $(NH_4)_2RbWP$, and K_2CsWP. Pure sodium or potassium salts are soluble, and alkali metal salts have properties similar to the parent dialkali hydrogen heteropoly salts. Other salts such as $(NH_4)_3WP$, Tl_3WP and Tl_2HWP were described by Krtil.[6] Most of these preparations exhibit strong base-exchange properties. The mixed salts of $H_3PW_{12}O_{40}$ with bi- or tervalent cations were prepared and the following composition was proved for them: $BaHWP$, $Ba_3(WP)_2$, $Ce(Cs_2WP)_3$, $Al(K_2WP)_3$, $Al[(NH_4)_2WP]_3$ and $UO_2(Cs_2WP)_2$.[21] The salts with quaternary organic cations have interesting properties. Pyridinium WP, picolinium WP, lutidinium WP, and collidinium WP salts are anhydrous and the positions of the isotherms for a particular exchanging cation such as NH_4^+ suggest that the exchangeability decreases in the order pyridinium WP > picolinium WP > lutidinium WP > collidinium WP. The same order was proved for the MP salts. The exchangeability of picolinium WP for univalent cations decreases in the order $NH_4^+ > K^+ > Na^+ \approx Li^+$,[4] and for pyridinium WP in the order $Cs^+ > NH_4^+ > K^+ > Li^+ > Na^+$.[22] The crystal lattice in ammonium tungstophosphate is perhaps too compact to allow the entry of a large cation like collidinium, but loose enough to allow the pyridinium ion to exchange for NH_4^+. In collidinium WP the channels are no doubt large enough for the entry of NH_4^+, but the collidinium is too firmly bound to be replaced by NH_4^+.[4]

WP is a specific exchanger for Cs^+, with lower capacity than MP, *e.g.*, for ammonium WP it corresponds to 0·66 meq/g. Ammonium WP was therefore used for Rb^+, Cs^+, K^+, Tl^+ and Ag^+ separations.[12] Thallium salts are convenient for ^{137}Cs determination in solutions with high Na^+ and K^+ concentrations. Recoveries were 99% for extracting ^{137}Cs from solutions containing $\leqslant$ 128-fold excesses of Na^+ and $\leqslant$ 8-fold excesses of K^+ relative to the amount needed to replace Tl^+ completely from the sorbent.[24] Pyridinium WP is highly specific towards Cs^+. The slopes of the isotherms are widely different for NH_4^+, Cs^+ and K^+ as compared with Li^+ and Na^+ exchange, suggesting that the univalent ions can be separated with the help of this exchanger.[22] Cs^+, NH_4^+ and K^+ salts of tungstophosphoric acid were used for co-precipitating astatine.[19]

Other heteropoly acids

Tungstosilicates (WSi), derived from $H_4SiW_{12}O_{40}$, form M_4WSi, M_3HWSi, M_2H_2WSi, but no MH_3WSi salts,[5] where $M = Rb^+, Cs^+$. High resolution NMR spectra indicate the tetrabasic character of WSi (and similarly pentabasic character of tungstoboric acid).[25] The WS collidinium salt is insoluble, whereas the pyridinium, picolinium and lutidinium salts are soluble. Such cations as NH_4^+, K^+, Na^+, Li^+, Sr^{2+} and Al^{3+} replace collidinium negligibly. Ion-exchange occurs with $(CH_3)_4N^+$, $(CH_3)_3NH^+$ and $(CH_3)_2NH_2^+$ cations and the exchangeability decreases in the series $(CH_3)_4N^+ > (CH_3)_3NH^+ > (CH_3)_2NH_2^+$.[4] Whatman No. 4 paper impregnated with ammonium WSi was used for chromatographic separations of UO_2^{2+} from Bi^{3+}, La^{3+}, Cs^+, Eu^{3+} and Co^{2+}, and of Sr^{2+} from Y^{3+}. This method was designed for fission product and uranium ore analysis.[26]

Ammonium salts of molybdoarsenic and tungstoarsenic heteropoly acids as high-capacity cation-exchangers were applied to Rb^+, Cs^+, K^+, Tl^+ and Ag^+ separation.[12]

The quinine salt of molybdovanadophosphoric acid $H_3PMo_{10}V_2O_{39}$ was prepared as an electron exchanger. The total dynamic oxidation capacity with respect to Fe^{2+} and ascorbic acid was found to be 0·570 and 0·770 meq/g, respectively.[27] The molybdovanadosilicate of nitron(L) corresponding to the formula $(LH)_6SiMo_{10}V_2O_{40}\cdot H_2O$ also shows electron-exchange properties and was tested for its dynamic electron-exchange capacity with respect to $K_2Cr_2O_7$ and ascorbic acid.[28]

Oxine and pyridine salts of molybdogermanic acid were applied as thin-layers for the separation of uranium and fission products. Separations of Cs^+ from Zr/Nb, Ru, Sr/Y and Ce were performed in ammonium acetate–EDTA media.[29] A separation of Cs^+–Rb^+–K^+ and Na^+ by thin-layer electrophoresis on these materials was successful.[16]

Isopoly acids

The ion-exchange properties of isopoly acids, which can be considered as heteropoly acids of hydrogen,[30] have been of limited interest till now. For the univalent salts of isopolytungstic acid the NMR spectra suggest the formulae $M_{10}^I(OH)_2W_{12}O_{38}\cdot nH_2O$ and $M_6^I(OH)_2W_{12}O_{36}\cdot nH_2O$.[25] However, for transition metal salts an 11-heteropolytungstic structure has been proved by X-ray diffraction measurements.[31] The ion-exchange capacity of the K^+ and NH_4^+ salts of C-phase polymolybdic acid is dependent on the cationic polarizability of the ingoing cation.[32]

INSOLUBLE FERROCYANIDES

The ion-exchange properties of a large number of insoluble ferrocyanides of various metals, *e.g.*, of Ag, Zn, Cd, Cu(II), Ni, Co(II), Pb, Mn(II), Fe(III), Bi, Ti, Zr, V, Mo, W, U(VI), have been studied. Among them the ferrocyanides of bivalent metals, or cations like UO_2^{2+} and TiO^{2+}, have been the most extensively studied materials.

By mixing of metal salt solutions with $H_4Fe(CN)_6$, $Na_4Fe(CN)_6$ or $K_4Fe(CN)_6$ solutions, precipitates of various composition are formed, depending upon the initial ratio of reacting components, acidity, and the order of mixing. Pure compounds (or their mixtures) of limiting composition $M_2^{II}[Fe(CN)_6]$, $M_2^{I}M^{II}[Fe(CN)_6]$ and $M_2^{I}M_3^{II}[Fe(CN)_6]_2$ with various amount of water of crystallization (often not stated) are reported for ferrocyanides of bivalent metals. The composition and empirical formulae of individual ferrocyanides reported to be ion-exchangers are summarized in Table I.

TABLE I.—COMPOSITION AND EXCHANGE CAPACITIES OF VARIOUS FERROCYANIDE ION-EXCHANGERS

Ferrocyanide	Composition	Capacity for Cs^+, *meq/g*	Reference	Notes
Ag	$Ag_4Fe(CN)_6$	1·1	54	
Zn	$Zn_2Fe(CN)_6$	6·1	41, 56, 57, 58	
	$H_2Zn_3[Fe(CN)_6]_2$		97	
	$Na_2Zn_3[Fe(CN)_6]_2$		56	
	$K_2Zn_3[Fe(CN)_6]_2$		57	
	$Cs_2ZnFe(CN)_6$		56	
Cd	$Cd_2Fe(CN)_6{\cdot}7H_2O$		98	
	$5Cd_2Fe(CN)_6{\cdot}4K_4Fe(CN)_6$		98	
Cu	$Cu_2Fe(CN)_6{\cdot}6\text{–}8H_2O$		35	
	$Cu_2Fe(CN)_6$	4·5	41,42,44,99,100	
	$H_2CuFe(CN)_6$		99	
Co	$Co_2Fe(CN)_6$	4·6	34,41,101	
	$K_2CoFe(CN)_6$		34	
	$H_2Co_3[Fe(CN)_6]_2$		101	
	$AHCo_3[Fe(CN)_6]_2$		66	A = amine
	$A_2Co_3[Fe(CN)_6]_2$		66	A = amine
Ni	$Ni_2Fe(CN)_6$	5·8	33, 41	
	$K_2NiFe(CN)_6{\cdot}3H_2O$		36	
	$M_4Ni_4[Fe(CN)_6]_3$	1·0–1·2	47, 48	M = Rb^+, K^+
	$M_6Ni[NiFe(CN)_6]_4$	3·0–5·0	50, 102	M = Na^+, K^+, Rb^+, NH_4^+
Mn(II)	$Mn_2Fe(CN)_6$		99	
	$H_2MnFe(CN)_6$		99	
Fe(III)	$M^{I}Fe^{III}[Fe(CN)_6]{\cdot}nH_2O$	3·6	41, 103	M = alkali metal ion
	$Cs_{16}Fe_4^{III}[Fe(CN)_6]_7{\cdot}nH_2O$		103	
Ti(IV)	$[(TiO)_2(OH)(HFe(CN)_6){\cdot}4H_2O]_n$	2·3	37	
V(V)	V:Fe = 3·86:1		62	prepared from $NaVO_3$
	V:Fe = 1·1	2·3	62	prepared from $VOCl_2$
Mo(VI)	$[H_4Fe(CN)_6(MoO_3(H_2O)_x)_{2\cdot2-2\cdot5}]_i$	3·85	38	denoted by FeMo(II)
	$[H_4Fe(CN)_6(MoO_3(H_2O)_x)_{3\cdot8-4\cdot5}]_i$		38	denoted by FeMo(IV)
W(VI)	W:Fe = 1·32:1	1·02	67	
	W:Fe = 2:1–12:1		60	
U(VI)	U:Fe = 1·6:1	1·25	65	

For ferrocyanides of bivalent metals a general formula of $M^{2+}[N^{2+}Fe(CN)_6]$ has been reported by Doležal and Kouřím,[33] where M and N may be different metals. The N^{2+} and Fe^{2+} ions are bound together by CN^- groups and the M^{2+} ions are placed in the free space of the structural lattice. The M^{2+} ions are exchangeable. The composition of ferrocyanides containing alkali metals is formulated[33] as $A_{2x}M_{1-x}[NFe(CN)_6]$, where A is the alkali ion and x can lie between 0 and 1. Similar formulations have been proposed[34] also for the cobalt ferrocyanides, $Co[CoFe(CN)_6]$ and $K_2[CoFe(CN)_6]$.

Few data are available on the structure of ferrocyanide ion-exchangers. A cubic lattice has been reported for $Cu_2Fe(CN)_6$, with $a = 10{\cdot}013$ Å,[35] $K_2NiFe(CN)_6$ with $a = 10{\cdot}07$ Å,[36] and titanium ferrocyanide with $a = 10{\cdot}27$ Å,[37] and a tetragonal lattice has been reported for $K_2CuFe(CN)_6$ with $a = b = 9{\cdot}85$ Å and $c = 10{\cdot}50$ Å.[36] Infrared and NMR measurements on titanium ferrocyanide[37] indicate the presence of free H_2O and OH groups in the dried precipitates. No evidence was found of the presence of a large amount of free protons in this compound and the maximum ratio of exchangeable protons to $Fe(CN)_6$ groups reached the value of 1. The formula of basic salt, given in Table I, was the best representation to fit the infrared and NMR data.[37]

X-Ray structural data of molybdenyl ferrocyanides[38] with Mo:Fe ratio 2–4·5 indicate a body-centred tetragonal unit cell with a variable c-axis. The unit cell of the FeMo(II) compound (Table I) has a tetragonal structure with $c/a > 1$ which becomes perfectly cubic for the FeMo(IV) compound and again tetragonal at still higher Mo/Fe ratios, but now with $c/a < 1$. Continuity in the X-ray spectra and the evolution of the unit cell with increasing Mo/Fe ratio is an indication that molybdenyl ferrocyanides of different composition contain the same structural elements with different arrangements in the unit cell. Thus the unit cell of FeMo(II) contains 2 $[Mo_6O_{22}H_{16}]^{8+}$ groups, 5 $Fe(CN)_6^{4-}$ groups and 36 H^+ ions, which, in agreement with the titration curves,[39] corresponds to 12 meq/g. The unit cell of FeMo(IV) contains two $[Mo_6O_{22}H_{16}]^{8+}$, one $[Mo_4O_{17}H_{12}]^{2+}$ and four $Fe(CN)_6^{4-}$ groups, bringing the total amount of inbuilt H^+ ions to 44 [16 are associated with $Fe(CN)_6^{4-}$ groups] per unit cell, corresponding to 12·7 meq/g. The structure of both the forms is relatively open, which permits a high rate of exchange reaction and a very fast ionic transfer.[38] It is suggested that the structure is made up of parallel ferrocyanide–molybdenyl sheets 14 Å apart, separated by a layer of protonated ferrocyanide ions. Such a structure may swell on hydration and resembles to some extent the clay minerals.[40]

Ferrocyanide ion-exchangers are stable towards mineral acids; in HCl media the optimum stability range is 0·01–2M HCl.[37,38] In contact with HNO_3 a slight oxidation of Fe(II) to Fe(III) occurs, in alkaline media progressive hydrolysis has been observed. The most stable exchangers towards HNO_3 are the ferrocyanides of Co,[34] Ni and Fe(III).[41] Cu and Co ferrocyanides are reported to be resistant to hard γ-radiation.[34,42]

Ferrocyanide ion-exchangers act as cation-exchangers with a high affinity for heavy alkali metal ions, especially for Cs^+. However, copper ferrocyanide also exhibits anion-exchange behaviour.[42] The affinity series $Cs^+ > Rb^+ > NH_4^+ \geqslant K^+ > Na^+$ was found for Cu, Zn, Ni, Fe(III) and Zr ferrocyanides.[33,43] Similar affinity series were found for $Cu_2Fe(CN)_6$—$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$,[44] Ti ferrocyanide—$Cs^+ > Rb^+ > K^+ > NH_4^+ > Li^+$,[37] Mo ferrocyanide—$Cs^+ >$

$H^+ > Rb^+ > K^+ > Na^+$[40] and W ferrocyanide—$Cs^+ > Rb^+ > NH_4^+ > Na^+ > H^+$.[45,46] Affinity series for bivalent ions have been reported for $Cu_2Fe(CN)_6$—Ba > Ca > Cd > Zn > Mg[44] and Ti ferrocyanide—Ba > Sr > Ca > Mg > Be.[37] Although practically all ferrocyanides are described as highly selective towards Cs^+, higher selectivity towards Ag^+ has been reported for $Cu_2Fe(CN)_6$.[44] Similarly, compounds of the $K_4Ni_4[Fe(CN)_6]_3$ and $M_6Ni[NiFe(CN)_6]_4$ ($M = Na^+, K^+, NH^+_4$) types were found to be highly selective for Rb^+.[47–50] It is interesting that these compounds adsorb Rb^+ by molecular adsorption from SO_4^{2-},[51] NO_2^-,[52] and $C_2O_4^{2-}$,[51] solutions.

According to the M^+–M^{2+} exchange isotherms measured for different ferrocyanides,[33] the maximum uptake of alkali metal cations increases in the series Fe(III) < Cu < Zn < Ni < Co ferrocyanides. The same series is valid also for the uptake of alkaline earth metal cations. It is interesting that the affinity series for Co ferrocyanide (derived from the maximum amount adsorbed) is the reverse of that ($NH_4^+ = K^+ > Rb^+ > Cs^+ > Na^+$) for other ferrocyanides. It is assumed[33] that the property which is responsible for the affinity of various ferrocyanides towards alkali metal ions is the intensity of the electrostatic field on the surface of the cation in the ferrocyanide. The lower the value of this intensity, the higher the affinity for alkali metal ions. The lowest value of field intensity is in the case of cobalt ferrocyanide, where the inversion of the alkali metal affinity series occurs.[33] This behaviour is formally similar to that of some polystyrene resins with a high degree of cross-linking or to aluminosilicate glasses with a high aluminium content, and could be explained by an interaction of ionic size, field intensity and hydration energy effects.[33] However, the results of other authors conflict to some extent with these suggestions, showing Co ferrocyanide as highly selective towards Cs^+.[34,53] Also the high Rb^+/K^+ separation factor (390)[54] does not agree with the above-mentioned affinity series for Co ferrocyanide.[33]

Exchange capacities of individual ferrocyanide ion-exchangers for Cs^+ are summarized in Table I. They depend strongly upon the method of preparation of the exchanger and differ sometimes from batch to batch. Very often the maximum values corresponding to the stoichiometrical formulae are not reached.[40,41,55]

The ion-exchange mechanism in ferrocyanides seems to be rather complicated and not yet quite clear. Thus X-ray data on ferrocyanides of bivalent metals show differences between the compounds of the $M_2^IM^{II}Fe(CN)_6$ (or $M_2^IM_3^{II}[Fe(CN)_6]_2$) and $M_2^{II}Fe(CN)_6$ types. For the former compounds with different M^I, the same diffraction patterns were found. It has been established that during the Cs^+/M^+ exchange process[44,56] only one phase is present. On the other hand, in Cs^+ exchange on $Zn_2Fe(CN)_6$ the presence of two phases [a mixture of $Zn_2Fe(CN)_6$ and $Cs_2ZnFe(CN)_6$] was found.[55,56] The structural rearrangement in the latter case may also explain the rather slower kinetics of exchange reactions on $Zn_2Fe(CN)_6$ in comparison with those on $M_2^IZnFe(CN)_6$.[57,58] However, more data on exchange kinetics would be necessary for deeper understanding of the mechanism of the adsorption processes. The exchange-reaction rate on Mo ferrocyanide is governed by two processes,[59] film and particle diffusion. The apparent diffusion coefficients show a difference of 2–3 orders of magnitude between the diffusion in the film surrounding the particles and in the solid phase. A difference of about 2 orders of magnitude exists also between the reaction rates of 1–1, 2–1 and 3–1 exchange reactions.[59] A pure particle-diffusion mechanism has been observed for Cs^+ exchange on W ferrocyanide.[60]

More data have been reported on ion-exchange tracer equilibria and exchange thermodynamics. The plots of log K_d *vs.* log $[H^+]$ or log $[NH_4^+]$ give straight lines with the slopes corresponding to the valency of the exchanged cation for Na^+, K^+, Rb^+ and Cs^+ exchange on Zn ferrocyanide,[61] Rb^+ and Cs^+ exchange on V ferrocyanide,[62] Cs^+, Co^{2+}, Sr^{2+}, Fe^{3+} and Ce^{3+} exchange on Mo ferrocyanide[39,63] and Na^+, Rb^+, Cs^+, NH_4^+, Sr^{2+} and Ce^{3+} exchange on W ferrocyanide.[45,46] The exchange equivalence has been proved for the K^+–Cs^+, Zn^{2+}–Cs^+ and Cs^+–Na^+ systems on Zn ferrocyanide.[56,57] Thermodynamic equilibrium constants and the corresponding ΔG values have been determined for Na^+, Rb^+, Cs^+, Sr^{2+} and Ba^{2+} exchange on Mo ferrocyanide.[40] The only negative ΔG value was found for Cs^+/H^+ exchange (-560 cal/mole). All these findings indicate a true ion-exchange mechanism. However, very often some irregularities in these dependences have been observed, where the slopes of the plots did not correspond to the valency of the exchanged cation[62,64,75] or the plots were far from linear.[64] In the case of Ti ferrocyanide the log K_d values for Cs^+ decreased even with increasing pH.[64] Furthermore, non-equivalent exchange was observed in some systems,[34,56,64,66] which has been explained by simultaneous adsorption of anions.[56] The mechanism of the adsorption of bivalent transition metals and some ter[5] and quadrivalent metals (forming insoluble ferrocyanides) will be even more complicated and the formation of the corresponding ferrocyanide sheets in the sorbent should be considered as in the case of Ni^{2+} and Co^{2+} adsorption on Mo ferrocyanide.[40]

The selectivity coefficients and separation factors determined for a series of systems and various ferrocyanides[43,45,54,62,64,65,67] have enabled various separation procedures to be worked out. Thus Zn ferrocyanide is suitable for the Na^+–K^+ and Rb^+–Cs^+ separations[61] as well as for the separation of Cs^+ from mixtures[58,68] of fission products. A rapid thin-layer chromatographic separation of Na^+, K^+, Rb^+ and Cs^+ on Zn ferrocyanide plates has been described.[69] A wide range of separation applications has been reported for Co ferrocyanides, especially for large-scale column isolation and concentration of ^{137}Cs from fission-product waste solutions,[34,53] ^{137}Cs separation from radioactive wastes and sea-water,[70] adsorption of traces of Cs^+ from oceanic fall-out,[71] and for the isolation of ^{137}Cs and its subsequent γ-ray spectrometric determination.[72] Ni and Cu ferrocyanides have been used for the treatment of liquid radioactive effluents from the Italian nuclear centre at Cassaccia.[73] Fe(III) ferrocyanide has been successfully used as an isotope generator to separate ^{137m}Ba from ^{137}Cs.[74] The possibility of separating fission products (Cs, Sr, rare earths, Zr) from uranyl salt solutions as well as of Th from U has been mentioned for Ti ferrocyanide.[64] V ferrocyanides[75–77] are suitable for Rb^+ and Cs^+ isolation from acid solutions and in the presence of NH_4^+ salts. The ^{137}Cs separation from fission products yields radiochemically pure ^{137}Cs.[77] The possibility of Cs^+ co-precipitation with Cu and Fe ferrocyanides being suitable for the removal of radiocaesium from low and high activity-level waste water[78] or for the removal of Cs^+ contaminants from simple aqueous solutions[79] has been discussed. Manganese and vanadyl ferrocyanides may also be used as ion-exchanging membranes.[80,81]

In order to improve the mechanical properties of ferrocyanide ion-exchangers for use in column operations, the preparation of the exchangers has been carried out by precipitation on solid inert supports, *e.g.*, bentonite, silica gel *etc*,[82–85] by freezing and thawing the precipitated gels,[86] or by binding the precipitate particles with insoluble polymers such as polyvinyl acetate.[87] The exchangers prepared in such a way behave in general similarly to the mother ferrocyanides, although some differences have been also reported,[83] such as higher capacity, resulting from the larger overall surface area of coarsely-grained supports.

Ferrocyanide/ion-exchange resins have recently become the most intensively studied metal salt/ion-exchange materials. They are prepared by treatment of strongly basic anion-exchange resins with metal salt and $K_4Fe(CN)_6$ solutions. Thus V, Ce, Cu, Ni, Co, Fe, Cd, Zn ferrocyanides[88–94] in combination with anion-exchangers AV-17, AN-9, Amberlite IRA-410, IRA-904, IR-45, IRS-50, A-27 and Dowex 1 × 10 have been prepared. The exchangers behave both as cation- and anion-exchangers[88,89] and are very stable towards acids, alkalies and hard γ-radiation.[88] The cation-exchange capacity is usually high, which is explained by the presence of the negatively charged complexes with the anion-exchanger functional groups of the type $\{[R_4NFe(CN)_6]_2Cu\}^{4-}$.[90] The formation of the complexes has been proved by X-ray and infrared measurements.[89,95] The exchange ability of individual ferrocyanides decreases with decreasing charge on the ferrocyanide complex cation ($V > Ce > Cd > Zn > Co = Cu > Fe > Ni$) and according to the anion-exchange resins used, in the order IRA-410 > IR-45 > AN-9.[89]

The resins are specific for ^{137}Cs[91] and mutual separation of fission products ^{137}Cs, ^{90}Sr, ^{95}Zr, ^{95}Nb, ^{106}Ru and ^{144}Ce has been achieved on Cu ferrocyanide–Amberlite IRA-904 resin in HCl media. Similar results were obtained with Fe(III) ferrocyanide from HNO_3 solutions.[93] Removal of caesium from radioactive effluents,[96] and separation of ^{137}Cs from ^{137}Ba for the purpose of ^{137}Ba preparation,[92] have been described.

SYNTHETIC ALUMINOSILICATES

Synthetic aluminosilicates represent a great family of inorganic ion-exchangers which, depending upon their structure, may be divided into three main groups: amorphous, two-dimensional layered aluminosilicates (synthetic analogues of clay minerals), and aluminosilicates with rigid, three-dimensional structures (zeolites). Although the ion-exchange properties of the first two groups have been studied in recent years,[104–107] attention has been concentrated predominantly on the third group of synthetic aluminosilicates, the synthetic zeolites.

Synthetic zeolites

During the last 15–20 years, the synthetic zeolites have attracted increasing attention because of their molecular- and ion-sieving properties, and have been successfully applied in gas-adsorption and catalysis. Some of these synthetic zeolites are analogues of zeolite minerals, but many new varieties have been prepared. The ion-exchange and ion-sieving properties of both synthetic and natural zeolites have been described in many excellent books, reviews and surveys;[2,108–118] the fundamental structural and ion-exchange studies are presented in a great number of papers from the laboratories of Barrer and Sherry. The developments of the last five years will be reviewed in this section. The zeolites are crystalline, cross-linked, polymeric aluminosilicates. The basic units of the polymeric macromolecules are $Si(O/2)_4$ and $Al(O/2)_4^-$ tetrahedra, where O/2 represents the bridging oxygen atoms. Each tetrahedron containing aluminium formally bears one unit of negative charge which is compensated by metal cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, *etc*, present in the interstices of the aluminosilicate framework. These cations are usually mobile and are responsible for the ion-exchange properties of zeolites. The remaining space in the interstices of the framework is filled by water or solvent molecules.[112] Besides aluminosilicate zeolites, zeolitic structures containing Ga^{3+} and Cr^{3+} instead of Al^{3+}, and Ge^{4+}, Be^{2+} and Mn^{4+} instead of Si^{4+} have also been synthetized.[113,119,120]

The chemical composition of zeolites is usually expressed by the formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]{\cdot}zH_2O$, where M = metal cation of valency n and y/x usually varies between 1 and 5. The portion in brackets discloses the framework composition.[113] Chemical composition and some properties of the main types of zeolite are given in Table II.

TABLE II.—SOME ZEOLITES AND THEIR PROPERTIES

Zeolite	Idealized unit cell contents	Free diameter of the largest channel, Å	Total ion-exchange capacity, *meq/g* (anhydrous)
Linde X	$Na_{85}[(AlO_2)_{85}(SiO_2)_{107}]{\cdot}256H_2O$	7·4	6·34
Linde Y	$Na_{52}[(AlO_2)_{52}(SiO_2)_{140}]{\cdot}256H_2O$	7·4	4·10
Linde A	$Na_{96}[(AlO_2)_{96}(SiO_2)_{96}]{\cdot}216H_2O$	4·1	7·04
ZK 4	$Na_9[(AlO_2)_9(SiO_2)_{15}]{\cdot}27H_2O$	4·1	5·50
ZK 5	$Na_{30}[(AlO_2)_{30}(SiO_2)_{66}]{\cdot}98H_2O$	3·8	4·57
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}]{\cdot}24H_2O$	6·7	2·62
Heulandite	$Ca_4[(AlO_2)_8(SiO_2)_{28}]{\cdot}24H_2O$	2·4–6·1	3·45
Clinoptilolite	$(Ca, Na_2, K_2)_3[(AlO_2)_6(SiO_2)_{30}]{\cdot}24H_2O$	4·1–6·2	2·64
Ferrierite	$(Na, K)_4Mg_2[(AlO_2)_6(SiO_2)_{30}(OH)_2]{\cdot}18H_2O$		3·39
Stilbite	$Na_2Ca_4[(AlO_2)_{10}(SiO_2)_{26}]{\cdot}28H_2O$		4·22
Chabazite	$Ca_2[(AlO_2)_4(SiO_2)_8]{\cdot}13H_2O$	3·7–4·2	4·95
Linde T(erionite)	$Na_8[(AlO_2)_8(SiO_2)_{28}]{\cdot}27H_2O$	3·5	3·43
Analcite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}]{\cdot}16H_2O$	2·8	4·95
Wairakite	$Ca[(AlO_2)_2(SiO_2)_4]{\cdot}2H_2O$		5·02
Phillipsite	$(K, Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}]{\cdot}20H_2O$	4·2–4·4	4·67
Yugawaralite	$Ca_4[(AlO_2)_8(SiO_2)_{20}]{\cdot}16H_2O$		3·57

The structure of the zeolite framework consists of a geometrical arrangement of linked (Si, AlO_4) tetrahedra forming secondary structural units, including 4-, 6-, 8-membered rings of tetrahedra, double rings of tetrahedra, several types of chain, sheets, and a variety of polyhedra. The larger polyhedra have substantial intrapolyhedral free volumes (called cages or cavities) in which guest molecules may reside, and where also the mobile exchangeable cations are usually sited. The faces of the polyhedral units include 4-, 6-, 8- and 12-membered rings (called windows) which themselves have free diameters allowing the ions (or guest molecules) to pass into or out of the polyhedra. Examples of cages encountered in zeolite structures are shown in Fig. 1. Most zeolites have cavities of more than one size and cations are often located in all kinds of cavities. The cavities may form one or two independent three-dimensional systems of cavities. However, there are some zeolites (*e.g.*, mordenite) that do not have three-dimensional cavity systems. In these zeolites the large cavities parallel to one axis are interconnected by smaller cavities which are not themselves interconnected.[112]

Synthetic aluminosilicates can be roughly divided into structurally defined groups, which can be related to their naturally-occurring analogues. For that reason we have classified all the material reviewed into the following groups: faujasite-, mordenite-, heulandite-, chabazite-, analcite- and phillipsite-like zeolites and other zeolites.

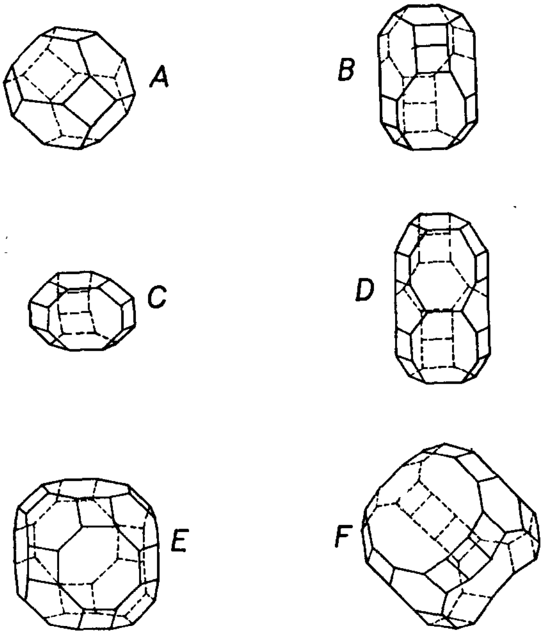


FIG. 1.—Diagrams of largest cavities in some zeolites.
A—sodalite, B—chabazite, C—gmelinite, D—erionite, E—Linde A, F—faujasite

The synthetic zeolites having no analogues in nature are mentioned either in the faujasite-like group (Linde A) or in the group of other zeolites.

Faujasite-like zeolites, zeolite Linde A

Of the wide range of synthetic zeolites, the zeolites of the faujasite group (Linde X, Linde Y) and zeolite Linde A have been the most extensively studied materials during the last five years.

Preparation, structure and chemical properties. These zeolites are usually prepared by hydrothermal treatment of sodium silicate, aluminate and hydroxide solutions[111,121–126] at temperatures of ~100°, or by mixing sodium silicate, aluminate and hydroxide solutions and evaporating till crystallization occurs.[127–133,366–368] Depending upon the ratio of reacting components, temperature, alkalinity and some other factors (the presence of binders, complexing agents, *etc.*[134–138]), products differing in chemical composition and properties (pore size, adsorption activity) are formed.

The faujasite-like zeolites Linde X and Linde Y (for chemical composition see Table II) have a common framework of the mineral faujasite and differ in the Si/Al ratio. The framework is formed[112] by stacking the cubo-octahedra (sodalite cages) by linking adjacent rings of 6 tetrahedra in a tetrahedral array similar to a diamond lattice. A part of the faujasite lattice is shown in Fig. 2. This arrangement forms two networks of cavities.[139,140] One network consists of large cavities, usually called supercages, with diameter ~12 Å. They are linked in a tetrahedral array by sharing rings of 12 tetrahedra. These rings (windows) have a face diameter of 8 Å. The other network is formed by linking smaller cages, called sodalite cages (diameter ~7 Å) in 2 tetrahedral array, through adjoining rings of 6 tetrahedra, thus forming secondary cavities which are hexagonal prisms, between sodalite cages. The rings of 6 tetrahedra form windows (free diameter $\sim$2·5 Å) between the sodalite cages and supercage. The faujasite lattice is a face-centered cubic lattice with octahedral symmetry, with a lattice parameter of 24·9 Å for Na–X.[112] However, the values of the lattice parameter are changed on changing the Si/Al ratio.[141] From the two breaks of the plot of lattice parameter against Si/Al ratio for a range of hydrated Na–X and Na–Y zeolites it has been concluded that in the Si/Al region between 1 and 1·4 the X-zeolite phase exists, the region between Si/Al $>$ 1·4:1 and Si/Al $<$ 2:1 represents transition between the X and Y phases, and at Si/Al = 2:1 the pure Y phase occurs.[141] The phase changes are due to changes in the Si–Al ordering in the 6-membered rings.[141] These phase-existence regions agree with the Si/Al ratios usually reported for the X (Si/Al = 1·1–1·5) and Y(Si/Al = 1·5–3·0) zeolites.[119,142] The Si/Al ratio in the zeolites, especially of the Y type, may be changed in different ways. The treatment of NaY zeolite with EDTA solutions leads to the removal of up to about 50% of the aluminium from the aluminosilicate. A highly crystalline product, with increased thermal stability and sorptive capacity, is thus prepared.[143,144] Also the extraction of Al_2O_3 by organic compounds leads to a material with an unchanged crystal lattice in which the acidity is characterized by a preponderance of sites corresponding to very strong acids. The aluminium sites removed by the extraction are those which give the zeolite a weak or intermediate acidity.[145] The aluminium component that is removable from the framework not only reduces the number of anionic sites when it is still present, but also occupies the cationic sites and thus decreases the ion-exchange capacity.[144]

The framework of the zeolite Linde A (Si/Al = 1·0) as well as of zeolite ZK-4 (1·0 $<$ Si/Al $<$ 1·7)[146] is formed by stacking the sodalite cages in a cubic array by linking a ring of 4 tetrahedra of the other cage. Double rings of 4 tetrahedra connect two sodalite cages, and the enclosed volume, the supercage, is the truncated cubo-octahedron (Fig. 1, E). The rings of 4 tetrahedra are too small to permit passage of ions or molecules. Thus the Linde A structure, a part of which is shown in Fig. 3, contains only one three-dimensional network of large cavities formed by connecting supercages through shared rings of 8 tetrahedra.[112] Isolated sodalite cages open out into supercages through shared rings of 6 tetrahedra.

If the truncated cubo-octahedra are linked in 8-fold co-ordination through their 8 × 6 rings the framework of the zeolite ZK-5 is formed. The bonds then form hexagonal prism units. By this arrangement additional 18-hedral cavities are created, having 12 × 4 ring and 6 × 8 ring faces.[109,147]

A lot of work has been carried out on investigating the position of various cations and water within the framework of these zeolites,[113,140,148] which is important for understanding the ion-exchange and ion-sieving properties of these materials. In the zeolite Na-X there are 38 Na^+ ions in large cavities and since they cannot be located by X-ray technique, they are presumed to be mobile completely hydrated counter-ions (Type III).[139,140] The MPR and NMR measurements suggest that these ions form with water a so-called "cationic solution".[149–151] The hydration number of cations in this solution is approximately equal to that in aqueous solutions. A further 32 Na^+ ions are located near the centre of the rings of 6 tetrahedra which interconnect the supercages and the sodalite cages, slightly displaced into the supercage (Type II). These ions are partially co-ordinated with water molecules. The remaining 16 Na^+ ions are located either in the hexagonal prism or in the sodalite cages (Type

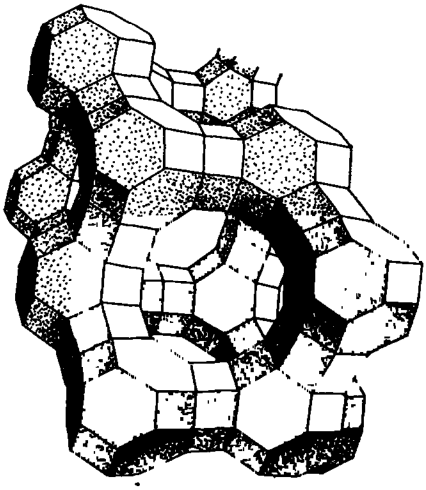


FIG. 2.—Arrangement of sodalite cages or cubo-octahedra to give faujasite type. Reprinted from Ref. 112, p. 96, by courtesy of Marcel Dekker, Inc.

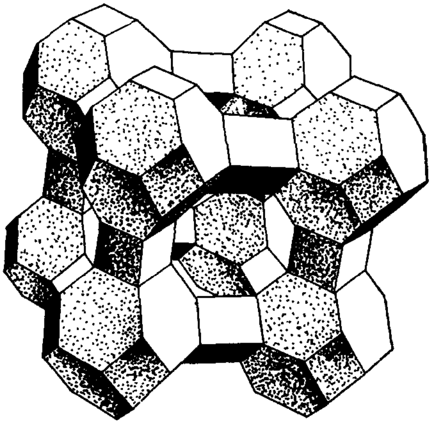


FIG. 3.—Arrangement of sodalite cages or cubo-octahedra to give Linde A. Reprinted from Ref. 112, p. 96, by courtesy of Marcel Dekker, Inc.

I).[139,140] A similar Na^+ distribution has been found for the Na–Y zeolite, but the majority of cations in the supercages are probably completely hydrated and non-sited.[139] However, a recent reinvestigation by X-ray diffraction of the Na–X zeolite structure[152] as well as the calculations of Madelung's potentials[153] led to a little different distribution of Na^+ ions (see Table III, Fig. 4.). The main difference is in dividing the type I Na^+ ions into two sites (I and I′), with 9 Na^+ ions occupying the centres of hexagonal prisms and 8 Na^+ ions lying on the inside of the sodalite cage opposite site I, near the 6-membered rings. In site II 24 Na^+ ions and 8 H_2O have been found. The number of Na^+ ions in this site agrees exactly with the number of site II 6-rings that contain three Al^{3+} ions. A rule that has been suggested,[152] is that three Al^{3+} ions per 6-ring are required to make partial dehydration and ion-siting

TABLE III.—LOCATION AND DISTRIBUTION OF Na^+ CATIONS AND H_2O IN NaX

Site	Reference 140	Reference 152
I	16 Na^+	9 Na^+
I′	0	8 Na^+ + 12 H_2O
II	32 Na^+	24 Na^+ + 8 H_2O
II′	0	26 H_2O
additional supercage sites	none located	127 H_2O (and Na^+)

Site I—centres of hexagonal prisms

Site I′—on the inside of sodalite cage opposite site I, near the six-membered ring

Site II—on six-ring faces of sodalite units, on the large cavity side

Site II′—within the sodalite cage opposite to site II

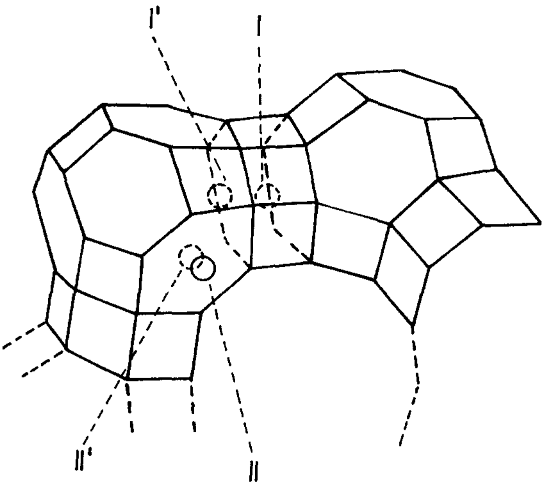


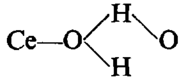
FIG. 4.—Schematic illustration of cation positions in Linde X. Designation of the sites is the same as in Table III.

energetically favourable. This rule will probably be valid for all zeolites that are sufficiently open to provide a choice between siting of partially dehydrated ions and non-localization of fully hydrated cations.[152]

Similar location of Na^+ ions has been found in the Na–A type zeolites. Eight Na^+ ions were located in the six-membered rings separating the large and small cavities (one in each of the 8 rings in a unit cell,)[140,154] the others were not been located and were presumed to be "dissolved" in the zeolitic water. However, their location has recently been found[155] in the plane of the 8-membered rings near the edge of the opening of the framework cavity.

Besides X-ray diffraction, ESR,[156–158] PMR[159] and Mössbauer spectra[160–163] measurements have been applied to the determination of siting of bi- and tervalent cations in these zeolites. Generally, the cation siting depends on the nature of the cations present, ionic charge and radius, degree of covalent character of the cation bonding, and on the water content.[164] The dependence of the various site occupancies upon the water content is evident for bivalent-cation faujasitic zeolites, where the occupancies of I′, II′ and I sites are a linear function of the site II′ water content.[165]

Dehydration of the zeolites causes changes in cation locations,[166–179] such as localization of non-located cations[180,181] and their concentration in sites within the sodalite cages.[164,182,183]

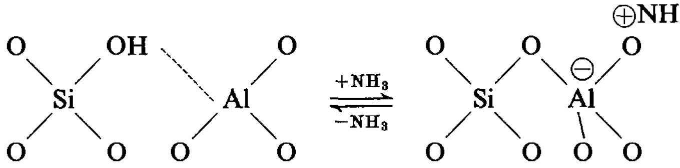
The dehydration of zeolites is thus highly dependent on their ionic forms. Generally, the thermal stability increases with enhancement of the Si content in the zeolites. For the same type of zeolite this increase depends also on the size of the cation present.[184] The tervalent rare-earth ions occupy, as partially dehydrated ions, the 6-membered ring sites in the large cavity of the X-zeolite;[183] in the natural faujasites all rare-earth ions are in the supercage, with partial occupancy of the site located in the centre of the 12-membered ring.[183] The Ce^{3+} ions are held in that position by hydrogen-bonding of the type  $Ce{-}O\langle^{H\cdots O}_{H}$.[185]

The water content is an important factor in determining the ion-exchange properties of the zeolites. The water and the cations in the most open zeolites of faujasite type and of Linde A possess many of the properties of an electrolyte solution.[112] This solution also contains imbibed neutral salt "molecules." The imbibement obeys the Donnan distribution law.[186] For the largest inclusions the average number of anions was between 3 and 4 chloride ions per large cavity of Li^+–X. The cations of the imbibed salt may occupy certain preferred sites within the zeolite framework and would then behave indistinguishably from similarly located lattice cations. The number of these preferred sites may be greater than the number of cations needed for electrical neutrality.[186] The majority (about $\frac{2}{3}$) of the water is present as a liquid phase of high mobility[187] filling the framework cavities. The electrical conductivity of the X- and Y-zeolites is comparable to that of aqueous electrolyte solutions and is attributed to the cations present in the supercages.[188] The remaining part of the water is bonded with freely-moving or located cations[187,189,190] or forms hydrogen-bonds with oxygen atoms of the cavity windows.[187] However, the presence of OH groups has also been identified by the infrared spectra measurements. These groups are sometimes resistant to high temperatures (~500°) and may be ascribed to surface OH groups,[189,191,192] cation-deficiency OH groups,[189,193] or defective-site OH groups.[189] The dehydrated zeolites contain also OH groups, as Al–OH and Si–OH groups.[189,191] The dehydration leads also to a positioning of the residual water.[133,194] The partially dehydrated bi-and tervalent ion forms of these zeolites contain also structural OH groups, forming the M^{II}–OH^+[195–200] or M^{III}–OH^{2+} groups.[196] The presence and positioning of the OH groups is an important factor determining the catalytic and adsorptive activity of these zeolites.

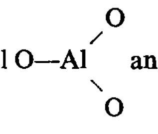
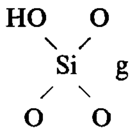
Various cationic forms of the X, Y and A type zeolites are prepared by an ion-exchange treatment of the basic Na^+ form,[112,201–203] by hydrothermal synthesis in the presence of components containing the desired cation,[204–206] or by contacting mother liquor slurries of the zeolite crystals with a cation-exchange resin in the desired cationic form.[207] Introduction of various cations into the basic Na^+ forms of these zeolites causes changes in their lattice parameters,[125,208–210] in window diameters,[211,212] in pore size,[213,214,369] and in electrostatic field strength.[215] Sometimes deformation and destruction of the crystal lattice occur.[199,209,211,216] Various cationic forms of the same structural type of the zeolite differ in their thermal, hydrolytic, and radiation stability,[217–224] as well as in the catalytic and adsorptive activity.[130,184,211,222,225–243] The details are outside the scope of this Review.

Decationized zeolites. The decationized forms of synthetic aluminosilicates have been widely applied in catalysis. However, the decationation process is rather complicated and the quality of the final products is highly dependent on the mode of preparation. The decationation by an ion-exchange process leads to partial zeolite decomposition if the conditions for the conversion are not carefully observed or the degree of conversion is overstepped.[244] Zeolites of high catalytic activity and of good stability have been prepared by selective replacement of the "cage" alkali metals by H^+, without replacing the "bridge" alkali metal cations.[226] In this way the hydroxyl groups are formed by replacement of the most readily exchangeable Na^+ ions located in the sites II and III (elsewhere in the supercage).[245] The destruction of NH_4^+-form zeolites, prepared usually by ion-exchange conversion,[246] has been proposed as one of the most convenient methods for the preparation of decationized zeolites[119] (besides the method of electrodialysis).

The NH_4^+-form of the A- and X-type zeolites exhibits maximum adsorption for H_2O vapour after thermal treatment at 100–150°. The NH_4^+-form of Y-type zeolite exhibits such a maximum on heating of the sorbent to 300°.[247] The thermal decationation of an NH_4^+–Y zeolite leads to the same products as the treatment of an Na^+–Y zeolite with HCl. Both products exist in the OH-forms. In the completely dehydroxylated form, 50% of the Al remains in 4-fold co-ordination, shown by a 50% retention of its initial ion-exchange capacity. The 3-fold co-ordinated Al is reconverted into the 4-fold co-ordinated form by the controlled addition of H_2O at elevated temperatures.[248] The maximum concentration of OH groups was obtained by heating the NH_4^+–Y zeolite at 350°. According to Kerr,[249] Ward,[250] and Uytterhoeven *et al.*[251] the hydroxyl groups are the Brønsted acid centres whereas the 3-co-ordinated Al atoms formed by a partial dehydroxylation of the zeolite are the Lewis centres. The formation of the Brønsted acid sites may be represented by the following reaction.[252]



By heating at 480° the Na^+–Y zeolite is converted into the Brønsted acid form. The concentration of these acidic sites increases linearly with decrease in the Na^+ content. After 60–70% of the Na^+ ions have been replaced, the concentration of these Brønsted acidity sites remains constant.[253]

The nature of the hydroxyl groups present in the decationized species was extensively studied by infrared spectra measurements.[248,252,254–262] Protons freed by zeolite decationation react with Si–O–Al bonds to form a trigonal  $\mathrm{O{-}Al}\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$ and an adjacent  $\genfrac{}{}{0pt}{}{\mathrm{HO}\ \ \mathrm{O}}{}\!\!\mathrm{Si}\!\!\genfrac{}{}{0pt}{}{}{\mathrm{O}\ \ \mathrm{O}}$ group.[263] The location of these hydroxyl groups is not exactly known, but it is probable that they have different locations in the truncated octahedra sections of the structure.[264] Two or three types of surface hydroxyl groups were detected in the decationized Y-zeolite.[259,260] One type is located on oxygens forming the bridge between adjacent cubo-octahedra, the second is located on the 6-membered ring of oxygen ions in the cubo-octahedron.[265–268] The decationation process leads to the easier release of the molecular water of the X- and Y-type zeolites.[258] Half the protons present in the decationized Y-zeolite correspond to the adsorbed molecular water.[269] High thermal stabilities were found for the fully decationized hydrogen zeolites, probably as the result of a general structural rearrangement. Thus the hydrogen form of zeolite Y, when heated to 700–800°, contained only 175 Si + Al tetrahedra per unit cell as compared with the 192 in faujasite.[270] The same zeolite may undergo a reaction with ammonia at 500°, yielding a highly stable product.[271] The preparation of an ultrastable form of faujasite free from metal cations is described, stable even at temperatures $>1000°$.[272]

Ion-exchange equilibria in faujasite-like zeolites. The ion-exchange equilibria in the X- and Y-zeolites have been intensively studied, especially for univalent cations.[139,273–275] In the zeolite Na^+–X, first the 37 non-located hydrated Na^+ ions, then the 32 partially hydrated site II Na^+ ions, and finally the 16 Na^+ ions located in the hexagonal prisms or sodalite cages are stepwise exchanged.[139] The ion-exchange isotherms of the K^+–Na^+, Rb^+–Na^+, and Cs^+–Na^+ systems show a selectivity reversal which is explained as follows: the first 37 (*i.e.*, up to ~40% exchange) non-located sites, on the basis of the hydrated ionic radii and coulombic interactions, should prefer all of the alkali metal cations (except Li^+). The selectivity series is thus as follows: $Ag^+ \gg Tl^+ > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The selectivity of the other two sites for counter-ions (where no H_2O molecules are interposed between the fixed anionic sites and the counter-ions) should be the net result of the opposing effects of the free energy due to coulombic interactions between the partially dehydrated counter-ion and the negatively charged lattice, and the free energy of partial ion dehydration. The selectivity series for the 32-fold set of sites is then $Ag^+ \gg Tl^+ > Na^+ > K^+ > Rb^+ \geqslant Cs^+ > Li^+$.[139] The 16 Na^+ ions in the hexagonal prisms or sodalite cages could not be exchanged by Rb^+ and Cs^+ owing to opening for entry being too small for the Rb^+ and Cs^+ ions to enter the sodalite cage. The Rb^+–Na^+ and Cs^+–Na^+ isotherms thus terminate at 82% exchange[139] (or even at 65% exchange).[276] The selectivity series for this set of sites is $Ag^+ > Tl^+ > Na^+ > K^+ > Li^+$.[139] The high selectivity towards Ag^+ and Tl^+[139,273] is consistent with the high polarizability of these ions and indicates strong binding by all types of anionic sites. However, some different affinity series have been also reported: $Rb^+ > Cs^+ > K^+ > Na^+ > Li^+$,[276] $Cs^+ \approx Rb^+ > K^+ > Na^+ > Li^+$,[273] and $K^+ > Na^+ \geqslant Rb^+ > NH_4^+ > Cs^+ > Li^+ > (CH_3)_2NH_2^+$.[277] The standard thermodynamic functions for the ion-exchange in the zeolite Na^+–X are summarized in Table IV. For the $\Delta H°$ values a decrease has been found with decreasing difference in the sizes of the exchanging cations.[278] However, the interpretation of the thermodynamic data is difficult, owing to the incompleteness of exchange in some systems, and for that reason the $\Delta H°$ and $\Delta G°$ values are hardly obtainable. Further, the entropy changes given in the Table are composed values, containing terms for ionic hydration entropy, net transfer of water into or out the zeolite during the ion-exchange reaction, ion-pair formation, change of the ionic hydration and some other factors.[112,273,274] The

TABLE IV.—STANDARD THERMODYNAMIC FUNCTIONS FOR ION-EXCHANGE IN NaX AT 25°C

System	Max. exchange, %	$\Delta G°$, *kcal/eq*	$\Delta H°$, *kcal/eq*	$\Delta S°$, *cal/mole/deg*	Reference
Li^+–Na^+	100	+1·35	+1·79	+1·48	276
	100	+1·60	—	—	139
K^+–Na^+	100	−0·19	−1·25	−3·56	276
	100	+0·14	—	—	139
Rb^+–Na^+	65	−1·30	−1·50	−0·67	276
	82	+0·14	—	—	139
Cs^+–Na^+	65	−0·78	−1·66	−0·29	276
	82	+0·09	—	—	139
Ag^+–Na^+	100	−2·52	—	—	139
Tl^+–Na^+	100	−1·84	—	—	139
Ca^{2+}–Na^+	100	−0·16	—	—	276
	100	−0·32	+1·20	+5·1	282
	77	—	+0·87	—	276
Sr^{2+}–Na^+	100	−0·71	—	—	276
	100	−0·74	+0·53	+4·3	282
	97	−1·18	—	—	290
	85	—	+1·38	—	276
Ba^{2+}–Na^+	82	−1·31	−0·43	+3·0	282
	82	−1·29	−0·11	—	283
	74	−1·13	—	—	276
	64	—	−0·11	—	276
	100	−0·94*	—	—	282
	82	−1·37†	—	—	282
	82–100	+1·08‡	—	—	282
Ce^{3+}–Na^+	82	−2·30	—	—	290
	82	−1·10	—	—	290

* —50°C, refers to complete exchange of all the Na^+ ions in all the cavities

† —50°C, refers to replacement of only the Na^+ ions in the large cages

‡ —50°C, refers to replacement of only the Na^+ ions in the small cages

contribution of these factors to the total entropy change is mostly distinguishable only with difficulty.

The ion-exchange isotherms for univalent ion exchange in the Na^+–Y zeolite terminate at ~70% exchange for Rb^+, Cs^+, Tl^+ and NH_4^+ ions[139,274] indicating that these ions are too large to penetrate the sodalite cages. The non-sigmoidal shape of the isotherms (up to 68% exchange) indicates no site heterogeneity in the supercages and the selectivity thus decreases in the order $Tl^+ > Ag^+ > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+$. The sites in the network of small cavities exhibit a selectivity pattern typical of a surface which binds ions tightly: $Ag^+ > Na^+ > K^+ > Li^+$;[139] $Ag^+ > K^+ > Na^+ > Li^+$.[274] In contradistinction to the Na^+–X zeolite, Tl^+ ions do not replace the 16 Na^+ cations in the sodalite cages of Na^+–Y. This difference in behaviour of Tl^+ in the more siliceous form (Na^+–Y) of synthetic faujasite is attributed to the lattice contraction which occurs when SiO_2 replaces $NaAlO_2$.[139] The values of the standard thermodynamic functions for ion-exchange in the zeolite Na^+–Y are summarized in Table V.

The exchange of organic cations, such as $MeNH_3^+$, $EtNH_3^+$, $PrNH_3^+$, $BuNH_3^+$, $C_5H_{11}N^+$, $C_6H_{14}N^+$, $PhNH_3^+$, p-$C_7H_{10}N^+$, $C_5N_5N^+$ and $PhCH_2NH_3^+$ is limited by available cavity volume and steric effects. Selectivity due to affinity of zeolite lattice for protons dominates over the steric factors.[279] The maximum extent of exchange decreased with increasing molecular weight and polarizability of these cations.[280]

TABLE V.—STANDARD THERMODYNAMIC FUNCTIONS FOR ION-EXCHANGE IN NaY AT 25°C

System	Max. exchange, %	$\Delta G°$, *kcal/eq*	$\Delta H°$, *kcal/eq*	$\Delta S°$, *cal/mole/deg*	Reference
Li^+–Na^+	100	+2·86	+1·35	−5·05	274
	100	+2·70	—	—	139
K^+–Na^+	100	−0·37	−1·44	—	274
	100	−0·19	—	—	139
Rb^+–Na^+	69	−1·06	1·22	−0·53	274
	68	−1·30	—	—	139
Cs^+–Na^+	72	−1·42	−1·61	+0·63	274
	68	−1·46	—	—	139
NH_4^+–Na^+	68	−0·66	—	—	139
Ag^+–Na^+	100	−1·08	−0·50	+1·94	274
	100	−1·10	—	—	139
Tl^+–Na^+	69	−1·49	−1·38	+0·37	274
	68	−1·63	—	—	139
Ca^{2+}–Na^+	68	−0·42	+0·64	+3·6	282
	65	—	+1·04	—	274
	72	+0·17	—	—	274
Sr^{2+}–Na^+	68	−0·51	+1·54	+6·9	282
	69	+0·13	+0·96	—	274
Ba^{2+}–Na^+	68	−0·87	−0·35	+1·8	282
	69	−0·39	−0·03	—	274

The hydrogen forms of zeolites X and Y show irreversible changes of the crystal lattice when H^+ is exchanged for Na^+.[281]

The bivalent ion exchange equilibria in the zeolites X and Y have been studied for the Ca^{2+}–Na^+, Sr^{2+}–Na^+, Ba^{2+}–Na^+,[274,275,282–286] Cd^{2+}–Na^+ and Zn^{2+}–Na^+[287] systems. The ion-exchange isotherms for zeolite Na^+–X show 100% exchange of Ca^{2+} and Sr^{2+} at 25 and 50°, and of Ba^{2+} at 50°.[282] The Ba^{2+}–Na^+ isotherms at 25° terminate at 82% exchange for Na^+–X,[283] at 68% exchange for Na^+–Y.[282] The same value has been obtained also in the Ca^{2+}–Na^+ and Sr^{2+}–Na^+ systems on Na^+–Y[274,282] at 25°. Some examples of the exchange isotherms are shown in Fig. 5. The sigmoidal shape of the isotherms in the case of zeolite X is interpreted in terms of two different equilibrium constants (>1 and <1) for the exchange of supercage Na^+ ions and sodalite-cage Na^+ ions respectively. These two constants have been evaluated for the Ba^{2+}–Na^+–X system[282] and are presented (as $\Delta G°$ values) in Table IV. In the case of the Sr^{2+}–Na^+ system an unusual shape of the exchange isotherms has been found, which arises from limited miscibility of the end-members Na^+–X and Sr^{2+}–X. At a fixed aqueous solution composition, two solid phases co-exist.[288] Even if 100% exchange has been reached in the zeolite Na^+–X, the replacement of the 16 Na^+ ions in the small cages is very slow[273,282] and the hydrated water of the ingoing cations should be at least partially stripped before these cations enter the small cages.[273,282] The values of the standard thermodynamic functions for bivalent ion exchange in the Na^+–X and Na^+–Y zeolites are summarized in Tables IV and V. It has been concluded from the thermodynamic data that in the case of Ca^{2+}–Na^+ and Sr^{2+}–Na^+ exchange in Na^+–X the reactions are entropy-directed and controlled by water-ion interactions in the aqueous solution phase.[282] A small enthalpy change in the Ba^{2+}–Na^+–X system indicates that there is no strong interaction between the Ba^{2+} ions and the framework.[283] Further, a net transfer of water from the zeolite phase to the solution takes place during the Ba^{2+}–Na^+ exchange.[282] In the zeolite Na^+–Y there is no

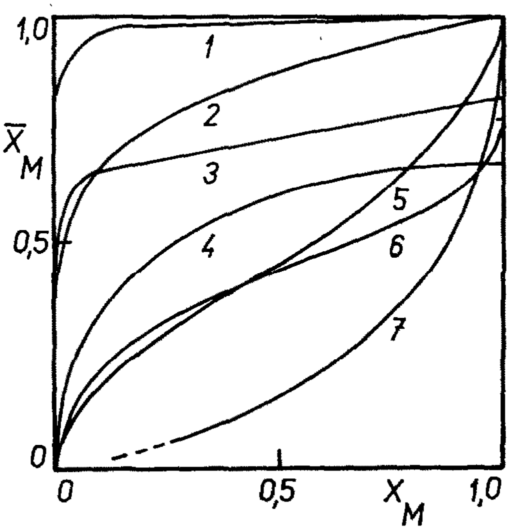


FIG. 5.—Some isotherms for ion-exchange on the Na^+–X, Na^+–Y and Na^+–A zeolites at 25°C.

X_M = equivalent fraction of M^{n+} ion in the solution
$\bar{X}_M$ = equivalent fraction of M^{n+} ion in the zeolite
1—system Ag^+–Na^+ for Na^+–A zeolite.[154]
2—system Tl^+–Na^+ for Na^+–X zeolite.[139]
3—system Ba^{2+}–Na^+ for Na^+–X zeolite.[282]
4—system Tl^+–Na^+ for Na^+–Y zeolite.[139]
5—system K^+–Na^+ for Na^+–X zeolite.[139]
6—system Cs^+–Na^+ for Na^+–X zeolite.[139]
7—system Li^+–Na^+ for Na^+–X zeolite.[139]

ion-siting in the large cages, so hydrated alkaline earth metal cations exchange for hydrated Na^+ cations.[282]

Reversible isotherms have been obtained by Sherry[289] and Ames[290] for the exchange of La^{3+} in Na^+–X and Na^+–Y as well as of Ce^{3+} and Y^{3+} in Na^+–X at 25°. The 16 Na^+ cations per unit cell in the network of small cages could not be replaced by these ions at 25°. However, at higher temperatures ($>80°$) a complete replacement occurred and the rate-controlling step in the replacement of the small-cage Na^+ ions was stripping of hydration water from the tervalent ions in the large cages.[289]

Equilibria in the Linde A zeolites. For the zeolite Linde A, the exchange isotherms and thermodynamic functions have been measured in many systems of uni- and bivalent cations.[154,284,291–295] The ion-exchange in the systems Li^+–Na^+, Cs^+–Na^+ and Ca^{2+}–Na^+ shows very marked energetic heterogeneity which is explained in the case of the Li^+–Na^+ system in terms of two sets of available sites. The first set accounts for 35–45% of all available ions (an average of 4–5 from the total 13 Na^+ ions per unit cell), while the remaining ions are associated with the second group of sites. However, larger ions such as Cs^+ are excluded for steric reasons from certain sites, at any rate from the sites located in or adjacent to the 6-membered rings.[291] Very often an excess of ion-exchange capacity of Linde A occurs owing to trapping of the AlO_2^- anion of the $NaAlO_2$ "molecule" occluded in the sodalite cage[112,292] during crystallization of the zeolite. This anion is too large to diffuse through the

2·6 Å window between the sodalite cage and the supercage. It has been found that there is one occluded $NaAlO_2$ "molecule" per sodalite cage which, together with the 12 AlO_2^- anions needed for the formation of the Linde A unit cell, is consistent with the unit cell formula of $Na_{12}[12AlO_2 \cdot 12SiO_2] \cdot NaAlO_2 \cdot 29H_2O$.[2] Larger cations such as Tl^+ and Ba^{2+} are unable to replace Na^+ ions from the sodalite cages and thus their isotherms terminate at 92 and 97% exchange.[112,154,296]

The following affinity series have been found for univalent cations: $Na^+ > K^+ > Rb^+ > Li^+ > Cs^+$,[291] $K^+ > Na^+ > NH_4^+ > Rb^+ > Cs^+ > Li^+ > (CH_3)_2NH_2^+$.[277] However, it is difficult to compare the affinity series found by various authors on various materials. The cation selectivity is a function of the anion charge-density[112] and thus a function of the anionic site separation distances.[297] As only the AlO_4 tetrahedra bear the negative charge of the framework an increasing SiO_2 content will enlarge the anionic site separation distances and decrease the anion charge-density.[112,297] Generally, the Na^+–A zeolite prefers cations of higher valency, atomic weight, polarizability, tendency to form ionic pairs, and ability to form more strongly dissociated complexes, but of lower tendency to hydrate in comparison with other cations of equal charge.[298,299]

TABLE VI.—STANDARD THERMODYNAMIC FUNCTIONS FOR ION-EXCHANGE IN NaA AT 25°C

System	Max. exchange, %	$\Delta G°$, *kcal/eq*	$\Delta H°$, *kcal/eq*	$\Delta S°$, *cal/mole/deg*	Reference
Li^+–Na^+	100	+1·30	+2·26	+3·2	291
K^+–Na^+	100	+0·14	−2·39	−8·5	291
Rb^+–Na^+	76	+0·68	−2·55	−11·4	291
Cs^+–Na^+	49	+1·98	−3·80	−19·4	291
Ag^+–Na^+	100	−3·93	−2·78	+3·9	154
Tl^+–Na^+	97	−2·32	—	—	154
Ca^{2+}–Na^+	100	−0·14	+2·10	+7·5	291
	100	−0·73	+2·70	+11·5	154
	100	−0·85	—	—	327
Sr^{2+}–Na^+	100	−1·01	+0·50	+5·1	154
	100	−1·30	—	—	327
Ba^{2+}–Na^+	97	−1·17	0	+3·9	154
Co^{2+}–Na^+	100	−1·63	—	—	301

The thermodynamic data for ion-exchange in the zeolite Linde A are summarized in Table VI. From the thermodynamic data it has been concluded that there is much ion-pair formation between cations and the fixed anionic sites in Ag^+–A and Ca^{2+}–A, less in Sr^{2+}–A, and almost none in Ba^{2+}–A.[154] No structural collapse has been found for the hydrated Ba^{2+} form of this zeolite[154,300] contrary to other observations,[296] and no structural changes have been found after the exchange of Co^{2+} for Na^+ ions.[301]

Ion exchange kinetics. The study of kinetics of processes on synthetic zeolites is very important from a practical as well as a theoretical point of view, because zeolites are amongst the few solids which show high ion mobility in a rigid and well defined crystal lattice. The diffusion kinetics of various cations in these materials show greater variety and complexity than they usually do for organic resins and thus attempt to correlate the kinetic and thermodynamic data with the nature of the cation, the restricting dimensions of the zeolitic framework, and the properties of solvent molecules, which is very useful for the deeper understanding of the ion-exchange processes on synthetic zeolites.

The alkali metal ions diffuse very quickly in the X-zeolite, and substantially faster than the bivalent cations. The values of the diffusion coefficients increase with increasing atomic weight for the elements of the same group.[302] The values of self-diffusion coefficients in the Linde A and X-zeolites for Na^+, Cs^+ and Sr^{2+} range from 1×10^{-9} to 5×10^{-7} cm²/sec in aqueous systems at 50°.[303] Sodium ions are, according to Dyer *et al.*,[304] freely mobile between the various sites even at low temperatures in the X- and Y-zeolites, but in the case of zeolite A, two unequal structural positions for Na^+, K^+, Rb^+ and Cs^+ were proved to exist by Hoinkis *et al.* from the self-diffusion data, even if the diffusion process of Na^+ and K^+ was extremely fast.[305,306] In the latter case, the distribution of Na^+, Cs^+ and Rb^+ over the different lattice types was found to be temperature-dependent.[128]

The self-diffusion coefficients of H_2O occluded in Na^+–X, Ca^{2+}–X and Ca^{2+}–Y zeolites were determined by pulsed field-gradient spin-echo NMR and corresponded to values of 1·34, 1·65 and $1{\cdot}88 \times 10^{-5}$ cm²/sec at 30°. The corresponding activation energies for self-diffusion were 6·9, 6·8 and 5·6 kcal/mole, respectively, and 5·04 kcal/mole for pure water. Thus there appears to be little difference between free water and water occluded in the zeolites.[307]

The self-diffusion and ion-exchange data for the systems Na^+–alkaline earth metal cations in X-, Y-, A- and ZK-4-type zeolites show considerable differences, which may be explained by the significant solvent-cation association in the case of bivalent ions.[306] The coulombic forces make the major contribution to the activation energies of these self-diffusion processes and thus the enhancement in the framework charge increases the self-diffusion energy.[284] The progress of a Ca^{2+}, Sr^{2+} or Ba^{2+}–water "complex" through the layer lattice window of the X-zeolite seems to be the rate-determining step.[166,308] For the Ba^{2+} ion, the diffusion energy barrier arises from the large bare ion moving from site I, through successive hexagonal windows out into the supercage. A much higher barrier exists for Sr^{2+}, which occupies site I′, in the zeolite X. Thus to gain a position in the large cavities, Sr^{2+} ions first have to lose their hydration sheaths before the ion passes through the hexagonal window of the sodalite unit.[309] Thus the increased values of activation energy would be explained by these high-energy barriers[166] increasing for the series $Ba^{2+} < Ca^{2+} < Sr^{2+}$.[308] On the other hand no ion-size effect has been noted for Sr^{2+}, Ca^{2+} and Ba^{2+} in this zeolite.[166,308] Also the values of entropy of activation can be indications of the differences in the diffusion path followed by Sr^{2+} and Ba^{2+}. The positive value associated with Sr^{2+} migration in zeolite X (137 J/mole/deg) would thus be a reflection of its restricted diffusion path and a large ion–water orientation. Conversely the negative value measured for Ba^{2+} migration (−66 J/mole/deg) is indicative of a comparatively higher degree of mobility and the lack of orientational effect which the ion has upon its water environment. The overall activation free-energy changes are nearly identical for both ion-diffusion processes (84 and 83 kJ/mole) which would seem to preclude structural changes as a contributory factor to Sr^{2+} self-diffusion in the zeolite X.[309] Bivalent cations such as Ca^{2+}, Sr^{2+} and Ba^{2+} experience difficulty in replacing a proportion of Na^+ ions, especially those in site I. However, if the temperature is raised to ~200°, the effect is to depopulate site I with respect to univalent ions in favour of bivalent ions. In these cases Sr^{2+} and Ba^{2+} occupy only one-half of the available site I positions.[304] The degree of conversion of X-zeolite into the bivalent form seems therefore to be the decisive factor for the diffusion phenomena. It has been shown that 80% of the exchangeable barium ions and 65% of the strontium ions have very high diffusion velocities in X zeolites, but the remainder diffuse only slowly, the diffusion coefficients differing by 4–5 orders of magnitude. The enthalpy of activation of the slower process is about twice that of the fast one. This is explained in terms of location of the ions in two types of channels, which are supposed to be separated from each other, each of them accommodating a certain proportion of the bivalent ions.[306,310]

Similar studies on bivalent cations were made with the A-type zeolites. In contrast to Cs^+ ions, the Sr^{2+} and Ba^{2+} distribution in A-zeolite is practically uniform.[306] For example, all six Sr^{2+} ions present per unit cell in zeolite A occupy structurally similar positions and the activation energy for self-diffusion was calculated as ~13 cal/mole/deg.[311] The self-diffusion measurements for Ca^{2+}, Sr^{2+} and Ba^{2+} illustrate the effect of increase in size of bivalent cations on the energy barriers for self-diffusion through type-A zeolites.[296] These cations are not completely surrounded by water molecules and some coulombic contribution to the energy barrier is of importance.[166] The rate-determining step for movement of the large Ba^{2+} ion through zeolites A, ZK-4 and chabazite is a sterically hindered process. The movement of Ca^{2+} and Sr^{2+} ions in chabazite and zeolite ZK-4 could be one in which the ion moves from a completely hydrated state through a restricting ring, losing part of its hydration envelope, and returns to its hydrated state on the other side of the ring.[308] Above 100°, the barium ion diffusion became an ideal diffusion process. At sufficiently high temperature all exchangeable cations leave their well-defined positions in the framework and are statistically distributed in the supercage.[312]

The use of non-aqueous solvents with lower dielectric constants and larger solvent molecules than water, has apparently little effect on the rate of Na^+ ion migration, the rate being extremely rapid even in zeolite A which has relatively small pore openings. The use of non-aqueous solvents has a considerable effect on the kinetics and thermodynamics of alkaline earth metal cation self-exchange processes.[284] The rate becomes immeasurably slow in zeolite A, and in zeolite X and Y there is a marked reduction in the self-diffusion rate and an increase in the activation energy with increasing size and decreasing dielectric constant of the solvent molecules. The effect of increasing size in an ion-solvent aggregate is the main cause of increasing energy barriers for self-diffusion.[284,313,314]

Mordenite-like zeolites

Natural mordenite $[(Ca,K_2,Na_2)O{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}6\text{–}7H_2O]$ has a well-known synthetic counterpart with a nearly rigid framework in all three dimensions, which is thermally stable and has a structure with various degrees of porosity (Zeolite AW-300, Zeolon[278]). Alkaline-earth varieties of this high-silica synthetic mordenite were prepared hydrothermally[315–317] by heating a mixture of SiO_2 and sodium aluminate with aqueous solutions of Na_2SiO_3 at 75–175°. The following formulae have been determined: $(Na,Ca/2)_2{\cdot}Al_2Si_9O_{22}{\cdot}2{\cdot}8H_2O$[315] and $(Na_2,K_2,Ca)Al_2Si_{10}{\cdot}O_{24}{\cdot}7H_2O$.[316] Mordenite crystals were prepared by prolonged autoclaving of the solutions with sodium silicate at 90–120°. The crystals contained a lower amount of Ca (<1% of

CaO) than that of natural mordenites (2–4 % of CaO).[318] The SiO_2/Al_2O_3 and Na^+/H^+ ratios in the mordenites can be changed without destroying their zeolitic structure. The Na^+- and H^+-forms of mordenites were prepared and their composition corresponded to $1{\cdot}04Na_2O{\cdot}Al_2O_3{\cdot}12{\cdot}2SiO_2$ and $2{\cdot}47H_2O{\cdot}0{\cdot}5Al_2O_3{\cdot}12{\cdot}2SiO_2$, respectively. Treatment of the Na^+-form with acids leads to ion-exchange and de-alumination processes. By the de-alumination the zeolite capacity is decreased and non-equivalent H^+ groups are formed. Heating of mordenite to ~400° causes deprotonation and de-alumination.[319]

Sorption phenomena on mordenites are closely related to the structural arrangement. The volume of two large channels (length ~7·52 Å) in the elementary unit cell of the synthetic mordenite was found to be 477 Å^3. The ions adsorbed are predominantly situated in the 12-membered oxygen windows. From these windows smaller channels formed by 8-membered windows branch out. The volumes of the large and small channels in the sodium (hydrogen) form of mordenite were found to be 0·0935(0·0980) and 0·0565 cm^3/g, respectively.[320] It was reasoned that if the zeolites were synthesized with a given ion in place, the structure should conform slightly to the spatial needs of the ion in question. If these ions are removed by ion-exchange, the zeolite should still retain a "frozen-in" structural preference for the original ions and thus an element of selectivity for this ion is built-in.[316] A strontium-selective mordenite can be prepared by this method.[321] PMR and infrared studies on synthetic mordenite have been performed.[322]

Heulandite-like zeolites

Naturally-occurring zeolites of the heulandite group are characterized by frameworks that tend to be lamellar. The minerals heulandite ($CaO{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}5H_2O$), clinoptilotite [$(Ca,Na_2,K_2)O{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}8H_2O$], stilbite [$(Na_2Ca)O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}6H_2O$], and ferrierite [$(Na_2,Mg)O{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}6H_2O$] have well-known synthetic analogues.[316,317,321,323–329]

Synthetic heulandite of the formula $(Na_2,Ca)O{\cdot}Al_2O_3{\cdot}7SiO_2{\cdot}H_2O$ gives the same X-ray data as the natural mineral. The basic volume of the zeolite is ~900 Å^3.[323] From NMR studies it is obvious that hydrogen enters the structure in the form of OH groups.[326] The high-silica zeolites of this group have been the most studied.

A synthetic heulandite–clinoptilotite zeolite was prepared hydrothermally by autoclaving at ~300° a mixture of LiOH, $Al(OH)_3$ and silica gel in the ratio of 1:1:12. A zeolite with the composition $11{\cdot}5SiO_2{\cdot}Al_2O_3{\cdot}0{\cdot}99Li_2O{\cdot}18{\cdot}9H_2O$ has been prepared, with capacities for Sr_2^+ and Ce^{3+} of 0·46 and 1·16 meq/g, respectively.[317,324] Alkaline earth varieties of high-silica clinoptilolite, *e.g.*, $Ca(Na,K)_4Al_6Si_{30}O_{72}{\cdot}24H_2O$,[316] can also be prepared hydrothermally and a Ba-clinoptilolite-like phase has been prepared reproducibly in this way.[316] Low alkalinity of the solutions favours the formation of high-silica compounds. Na^+-alkylammonium clinoptilolites were prepared by the ion-exchange conversion of Na^+-clinoptilolite. The ion-sieve effects and the groups of ions which can displace all or only some of the total Na^+ can be reconciled with the free dimensions of the windows giving access to the two kinds of channels in clinoptilolite, if this is assumed to have an aluminosilicate framework isostructural with that of heulandite. The kinetics proved fully compatible with intraparticle diffusion, but not with intracrystalline or film diffusion.[325] As in the case of mordenite, selectivity of clinoptilolite for Sr^{2+} can be incorporated by the localized perturbations of the Al–Si network due to the conformation of this network, during formation, to the spatial needs of the exchangeable cation. For the gross composition $SrO{\cdot}Al_2O_3{\cdot}7SiO_2$, the separation factor for Sr^{2+} decreases in the order clinoptilotite > mordenite > ferrierite > yugawaralite. The higher separation factors for Sr may be explained by their relation to the larger channels of ~6·6 Å in the case of mordenite and perhaps clinoptilolite.[321] Very low values of ion-exchange enthalpies were found for the systems Na^+–Sr^{2+}, Na^+–Ca^{2+} and Sr^{2+}–Ca^{2+}.[327]

Alkaline-earth high-silica ferrierite-like zeolite was prepared hydrothermally, with the composition $(Na,K)_4Mg_2Al_6Si_{30}O_{72}{\cdot}18H_2O$.[316] Synthetic products containing strontium, usually designated as Sr–D, have X-ray characteristics very similar to those of natural ferrierite.[329] The corresponding H^+, Na^+, K^+ and Ca^{2+} forms were prepared by the ion-exchange conversion of the Sr^{2+} form.[328] Similarly to mordenite and clinoptilolite, the "frozen-in" structures can be incorporated for the Sr^{2+}-selective ferrierite preparation.[321]

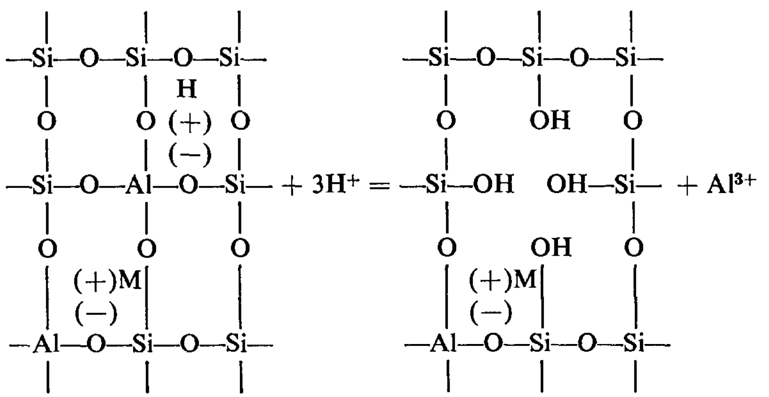
Chabazite-like zeolites

Chabazite-group minerals possess a rigid three-dimensional framework. Their structure may be represented by layer stacking, and the hexagonal prism units can be considered as the building blocks. Each zeolite of this group can be regarded as a sequence of layers of hexagonal prisms, the layers being firmly bonded to one another to give strong frameworks. Synthetic counterparts of natural chabazite $[(Ca,Na_2)O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}6H_2O]$, levynite $(CaO{\cdot}Al_2O_3{\cdot}3SiO_2{\cdot}5H_2O)$, and especially of erionite $[(Ca,Mg,Na_2,K_2)O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}6H_2O]$ have been described[278,322,327,330–340] From the X-ray studies of hydrated Ca-chabazite at +20 and −150°, three possible ordered arrangements of Si and Al atoms have been proposed.[330]

The chabazite-like synthetic zeolite AW-500 contains in its structure ellipsoidal cavities ~10 Å in free length and 6–7 Å in free diameter. Entry of either ionic or molecular species into these cavities occurs through one of the 6 eight-membered rings which form some of the polyhedral faces of each cavity. These rings are elliptical with maximum and minimum free diameters of 4·1 and 3·7 Å, respectively.[339] Free energies and enthalpies for the Na^+–Cs^+, K^+–Na^+ and K^+–Cs^+ ion-exchange reactions on chabazite-like synthetic zeolite AW-500 are very low and ΔH values diminish as the difference in the sizes of the exchanging cations decreases. The same conclusions were reached for the mordenite- and erionite-type synthetic zeolites AW-300 and AW-400.[278]

ZK-20 zeolite is isostructural with levynite. The composition corresponds to the formula $R_2O{\cdot}Na_2O{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}yH_2O$ with the components in ratios of 0·1–0·2:0·8–0·9:1·0:4·0–5·0, where $y = 1$–5 and R is the cation derived from 1-methyl-1 azonia-4-azobicyclo[2, 2, 2]octane silicate. The synthesis was carried out in the presence of sodium aluminate and at 80–120°.[331]

The erionite-like zeolite, designated usually as zeolite T, zeolite AW-400, or Linde T, has a hexagonal structure with $a = 13{\cdot}25$ Å, $c = 15{\cdot}12$ Å and density 2·07 g/cm³. The dimensions of the 8-membered windows are 3·5 × 4·7 Å and the cavity diameter corresponds to 6·3 Å. The number of these cavities is about $\frac{2}{3}$ that in chabazite.[335] From the electron-density map it has been concluded that the Na^+ and Ca^{2+} cations are placed in the large cavities.[338] Attempts to replace all K^+ ions from the pure potassium form of this zeolite indicate that 25% of the total cations, or one of the 4 cations per unit cell, are not exchangeable below 300°. Structural conditions make it likely that the non-exchangeable K^+ ion in each unit cell is placed in the small cancrinite cage.[333] The synthetic erionite of composition $0{\cdot}5K_2O{\cdot}5Na_2O{\cdot}Al_2O_3{\cdot}6{\cdot}6SiO_2{\cdot}5{\cdot}5H_2O$ does not lose its structure after replacement of the Na^+ and K^+ ions by H^+.[334,336] Univalent ions are preferred, sorption decreasing in the order $Cs^+ > Rb^+ > Ag^+ > K^+ \geqslant NH_4^+ > Na^+ > Li^+$, with large separation factors between adjacent alkali metal ions. It has been concluded that synthetic erionites prefer K^+ to Ba^{2+} and Ca^{2+} ions.[332,333] An inverse relation was noted between SiO_2/Al_2O_3 ratios and bivalent cation selectivities for the Na^+–Sr^{2+}, Na^+–Ca^{2+} and Sr^{2+}–Ca^{2+} ion-exchange equilibria.[327] Separation of heavy metals is also possible on these materials.[332] Synthetic erionites are stable up to 800°, which may be explained by the relatively high Si:Al ratio.[336] The prolonged treatment of erionite with an excess of dilute acids involves de-alumination; the Al lost thus may reach 40%. The process is expressed by the equation:



Over the temperature ranges 200–400° and 450–550°, these de-aluminated erionites release more water than exists in the starting materials. This is a direct verification of the existence of SiOH groups created by de-alumination.[336] Covalently bonded OH groups were found in the acid centres of decationized erionite. It is interesting, that compared with the original phase, an enhanced H_2O content in the H-centres was detected by PMR.[337]

Analcite-like and phillipsite-like zeolites

The analcite group contains two main minerals: analcite ($Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$) and wairakite ($CaO{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}2H_2O$). These possess a three-dimensional rigid framework and, like phillipsite [$(K_2,Ca)O{\cdot}Al_2O_3{\cdot}4SiO_2{\cdot}4\text{-}5H_2O$], they are characterized by the SiO_2/Al_2O_3 ratio usually ranging from 3·18 to 5·26. All these minerals have corresponding synthetic analogues.[316,327,341–346] Synthetic analcite[316] has an extremely slow rate of water self-diffusion and very high values of the corresponding activation energies[341] as compared with other zeolites. The extent of replacement of Na^+ ions by small bivalent or univalent cations exceeding a certain size is quite limited.[342] Synthetic wairakites[316] in the Sr^{2+}- and Ca^{2+}- forms prefer the univalent Na^+ cations to the bivalent Ca^{2+} and Sr^{2+} ions.[343] A phillipsite-like zeolite was prepared under precise hydrothermal conditions (to prevent the formation of faujasite).[344] Phillipsite is a zeolite closely related to zeolite B, which has the same composition as zeolite X.[345] Three different structures of sodium-phillipsite (NaP) synthetic zeolites may exist: (1) with primitive cell, where $a \geqslant c$, and the Li^+- and Na^+-forms are tetragonal and the Mg^{2+}-, Co^{2+}-, Ni^{2+} and Cu^{2+}-forms are cubic; (2) with body-centred cell, where $a > c$ and the K^+-, Rb^+-, Cs^+- and Ag^+-forms are tetragonal; (3) with body-centered cell, where $c \geqslant a$, and the Ca^{2+}-, Sr^{2+}- and Ba^{2+}-(Pb^{2+})-forms are tetragonal and the Cd^{2+}-form is cubic. The NaP-type zeolite containing $(K_2, Ca)^+$ and H^+ has a structure identical with that of natural phillipsite.[346] Very low ion-exchange enthalpies were found for the Na^+–Sr^{2+}, Na^+–Ca^{2+} and Sr^{2+}–Ca^{2+} ion-exchange reactions on synthetic phillipsite.[327]

Other zeolites

In this group there are included the remaining zeolites with counterparts in natural minerals, modified types of zeolites, and purely synthetic aluminosilicates without natural analogues.

The synthetic yugawaralite ($4CaAl_2Si_5O_{14}\cdot 4H_2O$)[316] and the synthetic zeolite Sr–Q[329] have X-ray characteristics very similar to those of the natural mineral. Potassium analogues of the sodium forms of synthetic sodalite-like zeolite Zh, with composition $Na_2O\cdot Al_2O_3\cdot 2\cdot 1SiO_2\cdot xH_2O$[347] cannot be prepared by direct synthesis. In the systems Na_2O–Al_2O_3–SiO_2–H_2O with Si/Al ratio 5, the zeolite Zh crystallizes at lowest SiO_2 contents.[122] From the electron-density map it was concluded that Na^+ ions in the zeolite Zh are placed in the centres of cubo-octahedral cavities. No ions were detected inside the 6-membered oxygen windows.[347] Hydrothermal syntheses were undertaken with the systems SiO_2–$Al(OH)_3$–NaOH–H_2O—anions for preparing synthetic zeolites which behave as anion-exchangers. Anions were formed when the NaOH/SiO_2 ratio was 0·5–3·0, for orthorhombic nepheline hydrate I in the presence of OH^- or F^-, or with cubic sodalite or one of its derivatives in the presence of Cl^-, Br^- or I^-, or with hexagonal derivatives of cancrinite in the presence of SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, NO_3^-, PO_4^{3-} or CO_3^{2-}. Much higher values of the NaOH/SiO_2 ratio caused formation of pure basic sodalite and hydroxyparacancrinite. These zeolites exchange OH^- groups with Cl^- anions at $>150°$.[348] Synthetic boehmite and pseudo-boemmite gels have been hydrothermally aged under acidic and neutral conditions.[349] Hydrothermal synthesis in the Li_2O–Al_2O_3–SiO_2 system leads to the formation of new zeolites. MCP II is an acid-resistant zeolite having a characteristic X-ray pattern, while MCP III is a layer-type mineral of the montmorillonite type, with possible composition $Li_2O\cdot(2Li_2O\cdot Al_2O_3)\cdot 8SiO_2\cdot xH_2O$, where the Li^+ ion appears as the exchangeable ion.[350] Zeolite L possesses a unique framework structure which has not been observed in any minerals. The structure has been tentatively ascribed to hexagonal β-tridymite. This zeolite has exceptional thermal stability and ability to exchange tervalent ions.[121] The zeolite of type Z-14HS was prepared by the paste method. This product retains a large percentage of its surface after steaming at 480–650°.[349] Modified zeolites have been prepared by treatment with multivalent elements, *e.g.*, zeolites with the general formula $(D_{2/n}O)_x$: MO_2:$(SiO_2)_y$ where D = univalent or bivalent metal, NH_4^+ or H^+, n = oxidation number of D, $x = 0\cdot 5$–$4\cdot 0$, M = Ti, Zr or Hf, and $y = 2$–10.[351] The zeolites with a high degree of Na^+-substitution were prepared by multiple treatment with saturated solutions of cations of group VI and VIII metals or the lanthanides and by subsequent heating at 140–550°.[352]

Practical ion-exchange applications of synthetic aluminosilicates

If the field of catalysis is excluded, relatively few interesting applications of the synthetic aluminosilicates have been suggested during the last five years. Most of these have been concerned with the removal of ions from waste solutions. ^{137}Cs may be recovered from fission-product wastes by zeolite ion-exchangers.[353] Mordenite- and erionite-like zeolites have been successful in the column separation of Cs^+ from the alkaline supernatant solutions in the Purex-process, desorption being effected by $3M\ (NH_4)_2CO_3$.[340] Two MCi of ^{137}Cs were recovered from Hanford wastes by an aluminosilicate ion-exchanger "Decalso".[354] Natural and synthetic aluminosilicate zeolites have been used for the removal of NH_4^+ in the presence of Ca^{2+}, Mg^{2+} and Na^+ ions from agricultural run-off and municipal waste-water.[355] Ag^+ can be separated from aqueous solutions by natural or synthetic aluminosilicates in the Na^+, K^+, or Na^+–K^+ forms. Ag^+ elution by concentrated NaCl or KCl solutions is possible without deterioration of the sorbent's ion-exchange properties.[356] The possibility of ^{137}Cs, ^{90}Sr and ^{91}Y removal from solutions containing variable amounts of humic acids has been studied on the Na^+–X type zeolite.[357] The zeolite 4–A was examined for adsorption of ^{137}Cs, ^{89}Sr, ^{60}Co and ^{106}Ru from NaCl solutions at $pH > 7$.[358] Separation of ^{106}Ru from ^{137}Cs, ^{152}Fe, ^{144}Ce and ^{60}Co on molecular sieve 4-A was successfully performed at pH 5.[359] The application of synthetic zeolites for removal of ruthenium from radioactive effluents has also been described.[360] Synthetic aluminosilicates MCPl, 2 and 3 were found to be effective adsorbents for radioactive waste disposal.[350]

Other practical applications are very limited. The cells of a solid-state battery, which perform satisfactorily even at 500°, utilize ion-exchanged crystalline zeolites as basic materials.[361] Papers containing crystalline zeolite particles[362] and ion-exchange membranes from natural or synthetic zeolites,[363] which were used for hyperfiltration and electrodialysis, have also been prepared. Zeolite applications in dissolution[364] and column chromatography[365] techniques are of secondary importance.

MISCELLANEOUS EXCHANGERS

Synthetic apatites

Various apatitic compounds have been studied with respect to their ion-exchange properties. Some of the anionic and cationic components of the apatitic structure $M_{10}(XO_4)_6Y$ are exchangeable, *e.g.*, where M = Ca, Sr, Ba, Cd and Pb, X = P, As, V, Cr(V), Mn(V), Si, Ge and Y = F_2, Cl_2, Br_2, $(OH)_2$, O and CO_3^{2-}. Hydroxyapatites containing Ca^{2+} ions and zeolitic water are the materials studied most.[370] Different methods of hydroxyapatite preparation are well known from the literature[371,372] and single crystals at least 1·4 mm in diameter can be prepared from single crystals of chloroapatite.[371] The structure, physicochemical properties, thermal stability, infrared spectra and ion-exchange properties of Ca^{2+}, Sr^{2+} and Ba^{2+} salts have been reported.[370] The adsorption of ^{45}Ca tracer on calcium hydroxyapatites, has been shown to proceed by a reversible iso-ionic exchange process at laboratory temperatures.[373] However, the ion-exchange of Ca^{2+} for univalent cations such as Li^+, Na^+, K^+ and Cs^+ was verified though the $(CH_3)_4N^+$ cation was found to be unexchangeable.[374]

Many authors have shown interest in OH–Cl exchange in these compounds. At lower temperatures, such an ion-exchange is impossible,[370,375–377] but at 250° and high pressure the exchange process occurs with limited reversibility and is dependent on the crystallographic parameter *a* of the sorbent,[375,376] on the chloride concentration in the system,[375] and on the Sr/(Pb + Sr) and Sr/(Ba + Sr) mole fraction.[376] The mixed Ca^{2+}–Ba^{2+} hydroxyapatite adsorbs chloride ions negligibly at higher temperatures. However, the process was found to be reversible.[377]

The presence of Na^+ and Pb^{2+} ions increases the exchange capacity for Cl^-. Na^+ ions favour the diffusion into the lattice channels by introducing vacancies at anionic sites. Pb^{2+} ions favour the diffusion into tunnels in the lattice as a result of the higher polarizability of Pb^{2+} relative to that of Sr^{2+} and Ba^{2+} ions.[376] On the other hand the presence of Na^+ ions gives rise to a shortening of lattice parameters as well as enhancing the exchange reversibility.[378] The compound $Sr_xPb_y($ [illegible] $_4)_6(OH)_2$ $(x + y = 10)$ sorbed Cl^- at room temperature and good reversibility of exchange was given by $Sr_3Pb_7(PO_4)_6(OH)_2$.[375] The exchange capacity for Na^+ was considerably increased by introducing Pb^{2+} ions into the alkaline earth hydroxyapatite lattice.[378]

OH–F exchange on synthetic and natural hydroxyapatites is facilitated by increase of the fluoride concentration and decrease in pH[370,379–381] and is strongly dependent upon the surface.[381] Non-stoichiometric compounds, *e.g.*, $Ca_{10}(PO_4)_6(OH,F)$, are formed,[379] and the exchange process is partially reversible.[377] Sodium monofluorophosphate is a less efficient agent than NaF for fluorinating the hydroxyapatites.[381] The first rapid stage of exchange is surface-dependent and the second slow stage may be diffusion-controlled.[380]

Two kinds of structural effects must be considered when trying to account for adsorption processes of the hydroxyapatites: those which are due to channels around the screw axis and those which are connected with the whole lattice. Occurrence of channels is connected with anisotropy of ionic conductivity, high diffusion rates along the channels, ion-exchange properties, and the ability of the apatitic lattice to fix some salts in the channel sites. The whole lattice arrangement enables CO_3^{2-} ions to be placed in sites out of the channels.[372]

The ion-exchange properties of strontium hydroxyapatites in the systems containing Na^+, Ca^{2+}, Ba^{2+} and Pb^{2+} ions have been described.[378] The OH^- content in these compounds is lower than the theoretical content and increases with decreasing content of Na^+ in the systems.

All problems connected with the synthesis, structure, structural properties and single-crystal preparation of fluoro, chloro and hydroxyapatites have been critically reviewed by Montel.[372]

Insoluble sulphides

The ion-exchange properties of a wide range of insoluble sulphides, *e.g.*, Ag_2S, FeS, CuS, ZnS, PbS, CdS, NiS, As_2S_3 and Sb_2S_3 have been studied in recent years.[382–386] These materials are usually prepared by precipitation from metal salt solutions with H_2S or Na_2S. Precipitation at low temperatures (70·5–253 K) leads to formation of granular materials with particle size increasing with decreasing temperature.[384,386,387]

The sulphides are selective towards cations forming insoluble sulphides. The exchange reaction proceeds primarily through metathetical reactions in which the metal of the sulphide is displaced by appropriate ions in the solution.[388] The exchange reactions are usually fast and can be carried out in small columns.[386,388,389] Quantitative adsorption of Pb^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Tl^{+} has been reported on ZnS, CdS and PbS,[389] of Pb^{2+}, Cd^{2+} and Cu^{2+} on NiS,[387] and of Cu^{2+} on ZnS and CdS. An equivalent exchange of the metal ion from the solution for the metal of the sulphides has been found.[387] The selectivity series for bivalent cations corresponded to the solubilities of freshly prepared amorphous sulphides.[389] On the other hand, no correspondence has been found with the solubilities of sulphide minerals.[383,389] The adsorption of Cu^{2+} on ZnS has been shown by X-ray measurements to proceed *via* formation of CuS. The limiting precipitate composition expressed by the formula NiS·2CuS has been found for the adsorption of Cu^{2+} on granular NiS.[390]

The rate and extent of conversion of the insoluble sulphides are determined by rates of diffusion of the pertinent ionic species in the solids. For example, the high reaction rates of Ag^{+} with most sulphides are connected with the large self-diffusion coefficient of Ag^{+} in Ag_2S.[388] However, some other processes such as physical adsorption[389] and oxidation-reduction processes[384] may accompany the ion-exchange reactions in these materials.

Alkaline earth sulphates

Special attention has been paid to materials based on the barium sulphate lattice. Two main applications of these materials have been studied. The first is the use of barium sulphate as a co-precipitation agent, where generally all positive ions of a charge >2 and an ionic radius larger than $\sim 1 \cdot 1$ Å are co-precipitated and can thus be isolated from solutions with 99% completeness or better. Although the exact adsorption mechanism is not clear, the strict dependence of efficiency on the ionic size and charge suggests isomorphous replacement in the $BaSO_4$ lattice.[391] However, the field of co-precipitation is well outside the scope of this Review. The second is based on the adsorption properties of barium sulphates with artificially introduced crystal-lattice defects.

Thus $BaSO_4$ preparations possessing enhanced sorption activity especially for Sr^{2+} have been prepared either by the partial metasomatic transformation of $CaSO_4$ into $BaSO_4$ by contacting the former with solutions of soluble barium salts, or by the heat treatment of the mixture of $BaSO_4$ and $CaSO_4$ above the $\beta \rightarrow \alpha$ transformation temperature (above 1000°), where both sulphates are miscible, with subsequent rapid chilling of the glowing mass in water.[392,393] These materials can also be prepared by the simultaneous precipitation of the insoluble sulphates from solutions of soluble barium salts containing salts of other metals, especially of calcium.[394] By the procedure involving the heat treatment, the metastable product is obtained with calcium sulphate fixed in the $BaSO_4$ lattice.[392,393] When placed in water, the weakly bound $CaSO_4$ component is eluted with consequent rapid recrystallization in the whole mass. During this process, ions, the sulphates of which are isomorphous with $BaSO_4$, are rapidly incorporated and thus may be removed from the solution. By the recrystallization and by the incorporation of these ions, the existing lattice stress is abolished, mixed crystals being formed.[392–395] The heat-treated and rapidly chilled product exhibits X-ray diffraction patterns and infrared absorption spectra characteristic of $BaSO_4$ only. No $CaSO_4$ features were detected.[392,396,397] At least a part of the $CaSO_4$ adopts the space group of the low-temperature (β) modification of $BaSO_4$.[396,397] The unit-cell parameters of the heat-treated sorbents (obtained by repeated recycling) are $a = 8{\cdot}480$, $b = 5{\cdot}397$, and $c = 6{\cdot}956$ Å, which are practically identical with the parameters of anglesite.[398] This coincidence of lattice parameters was suggested as a possible factor in promoting the selectivity for Sr^{2+}.[398] A nearly eutectoid mixture of $BaSO_4/CaSO_4 = 60/40$ mole % was found most convenient for preparation of the sorbents,[393,394,397,399] with the optimum cooling time 30 sec.[400] Different cooling media were examined, and thermal cycling facilitated formation of larger crystals.[400,401] Specific surface measurements of different preparations have been correlated with the adsorption abilities.[401] The radiation stability of these materials was found to be satisfactory but doses up to 5×10^9 rad caused a gradual decomposition into the original components.[402,403] Great attention has been paid to the sorption of Sr^{2+} on these materials in the presence of large amounts of Ca^{2+} ions.[393–395,399,401] The first stage of Sr^{2+} adsorption is a reversible ion-exchange process obeying the law of mass-action. The values of the diffusion coefficients and activation energies showed the existence of steric hindrance. The final stage of Sr^{2+} adsorption is an irreversible process.[392] Trace levels of Sr^{2+} were successfully separated from a large excess of Ca^{2+} ions under different conditions,[392,394,395] and practical applications in medicine and in waste-water decontamination on a pilot-plant scale were realized.[23]

CONCLUSION

In Parts I[1] and II of this Review we have attempted to cover as completely as possible the published papers in the field for the period 1965–70, both from the Western and Eastern countries, and especially those which are not easily available.

The number of materials which may be understood as inorganic ion-exchanging substances has grown enormously during the period reviewed. However, because the ion-exchange processes in many substances are accompanied by other phenomena such as physical adsorption, surface adsorption, precipitation and co-precipitation processes, lattice defects, *etc*, it has been difficult to find an exactly limited scope for the term "inorganic ion-exchanger." We have therefore included all the cases where at least some features of the ion-exchange process could be distinguished.

There appears to have been a marked trend towards providing a more exact explanation of ion-exchange reactions rather than studying purely practical separation applications. The basic studies of ion-exchange mechanisms have been carried out on defined crystalline materials, the detailed structures of which, along with the location of the exchanging ions in the crystal lattice, are of great interest. This knowledge, accompanied by the determination of the main thermodynamic functions, has permitted a full explanation of the ion exchange process. These studies have till now been carried out on synthetic zeolites and some acidic salts of multivalent metals. This tendency will probably also be extended to the other materials.

It is interesting that the ion-exchange process in many substances is connected with formation of defined insoluble compounds of the ingoing ion with the "matrix," and that the formation of two distinct solid phases has been detected in some cases. These facts together with the other observed phenomena mentioned above suggest that the ion-exchange processes in the case of inorganic ion-exchangers are of complex character and that the traditional treatment of these processes in terms of pure ion-exchange do not fully describe all aspects of the process.

Zusammenfassung—Ein Überblick über die Entwicklungen während der Jahre 1965–70 im Gebrauch von Salzen der Heteropolysäure, von Cyaneisenverbindungen und synthetischen Zeolithen als Ionenaustauscher.

Résumé—Une revue des développements durant la période 1965–1970 dans l'emploi des sels d'hétéropoly acides, de ferrocyanures et de zéolites synthétiques comme échangeurs d'ions.

REFERENCES

1. V. Veselý and V. Pekárek, *Talanta*, 1972, **19**, 219.
2. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
3. W. P. Thistlethwaite, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2143.
4. D. Choudhuri and S. K. Mukherjee, *ibid.* 1970, **32**, 1023.
5. T. V. Healy, *Radiochim. Acta*, 1964, **3**, 100.
6. J. Krtil and M. Chauko, *J. Chromatog.*, 1967, **27**, 460.
7. W. P. Thistlethwaite, *Chem. Soc. (London), Spec. Publ. No.* 22, 1967, 416.
8. J. van R. Smit, *J. Inorg. Nucl. Chem.*, 1965, **27**, 227.
9. C. J. Coetzee and E. F. C. H. Rohwer, *ibid*, 1970, **32**, 1711.
10. M. T. Ganzerli-Valentini, V. Maxia, M. A. Rollier and M. Barbaro-Forleo, *ibid.* 1970, **32**, 671.
11. M. T. Ganzerli-Valentini, V. Maxia and M. Barbaro-Forleo, *Radiochem. Radioanal. Lett.*, 1969, **2**, 225.
12. J. van R. Smit, *German Patent*, 1,210,416 (1966).
13. A. J. R. da Fonseca, M. H. D. de Matos and M. M. da Cruz Godinho, *Rev. Port. Quim.*, 1964, **6**, 17.
14. G. Oldham, A. R. Ware and D. J. Sykes, *Talanta*, 1969, **16**, 430.
15. K. Mountford and G. Oldham, *Loughborough Univ. Technol., Dept. Chem., Sum. Final Year Stud. Proj. Theses*, 1969 **10**, 46.
16. M. Lesigang-Buchtela and K Buchtela, *Mikrochim. Acta*, 1967, 1164.
17. S. D. Roy and M. S. Das, *Anal. Chim. Acta*, 1970, **51**, 509.
18. C. J. Coetzee and E. F. C. H. Rohwer, *ibid.*, 1969, **44**, 293.
19. Fu-Chun An, N. G. Krylov, Yu. V. Norseev, Tao-Nan Chao and V. A. Khalkin, *Soosazhdenie i Adsorbtsiya Radioaktivn. Elementov, Akad. Nauk SSSR, Otd. Obshch. i Tekhn. Khim.*, 1965, p. 80.
20. F. A. Belinskaya, E. A. Materova and A. I. Zub, *Issled. Svoistv Iono-obmen., Materialov, Akad. Nauk SSSR, Inst. Fiz. Khim.*, 1964, p. 198.
21. T. V. Healy, *Radiochim. Acta*, 1964, **3**, 106.
22. D. Choudhuri and S. K. Mukherjee, *J. Inorg. Nucl. Chem.*, 1968, **30**, 3091.
23. L. Berák, *Nuclear Res. Inst., Czech. Acad. Sci., Rept.* No. UJV 936 (1963.)
24. J. O. Francis and G. Oldham, *Loughborough Univ. Technol., Dept. Chem., Sum. Final Year Stud. Proj. Theses*, 1969, **10**, 23.
25. V. I. Spicyn, H. J. Lunk, V. F. Curvaev and I. D. Kolli, *Z. Anorg. Allgem. Chem.*, 1969, **370**, 191.
26. G. Marcu and L. Ghizdavu, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 1969, **14**, 39.
27. R. Ripan and A. Suteu, *Rev. Roumaine Chim.*, 1967, **12**, 1339.
28. *Idem, ibid.*, 1968, **13**, 179.
29. K. Buchtela and M. Lesigang, *Mikrochim. Acta*, 1965, 67.
30. E. A. Nikitina, *Geteropolisoedineniyia*, Gos. Nauch.-Tekhn. Izd. Khim. Literatury, Moscow 1962, p. 50.
31. R. Ripan and D. Stanescu, *Rev. Chim. Miner.*, 1967, **4**, 899.
32. H. Peters and K. H. Radeke, *Monatsber. Deut. Akad. Wiss. Berlin*, 1969, **11**, 351.
33. J. Doležal and V. Kouřím, *Radiochem. Radioanal. Lett.*, 1969, **1**, 295.
34. W. E. Prout, E. R. Russell and H. J. Groh, *J. Inorg. Nucl. Chem.*, 1965, **27**, 473.
35. M. L. Beasley and W. O. Milligan, *Trans. N.Y. Acad. Sci.*, 1969, **31**, 261.
36. P. J. Gellings, *J. Phys. Chem.*, 1967, **54**, 296.
37. K. A. Lieser, J. Bastian, A. B. H. Hecker and W. Hild, *J. Inorg. Nucl. Chem.*, 1967, **29**, 815.
38. L. H. Baetslé, D. van Deyck and D. Huys, *ibid.*, 1965, **27**, 683.
39. D. Huys and L. H. Baetslé, *ibid.*, 1965, **27**, 1329.
40. L. H. Baetslé, D. Huys and D. van Deyck, *ibid.*, 1966, **28**, 2385.
41. V. Kouřím, J. Rais and B. Million, *ibid.*, 1964, **26**, 1111.
42. E. V. Kazakov and I. F. Karpova, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1965, **20**, 95.
43. V. Kouřím, *Sb. Ref. Celostatni Radiochem. Konf.*, 3rd, *Liblice, Czech.*, 1964, p. 4.
44. E. V. Kazakov and I. F. Karpova, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1966, **21**, 139.

45. J. Krtil, *Sb. Ref. Celostatni Radiochem. Konf., 3rd, Liblice, Czech.*, 1964, p. 33.
46. J. Krtil, *J. Inorg. Nucl. Chem.*, 1965, **27**, 233.
47. V. V. Volkhin and S. A. Kolesova, *Zh. Prikl. Khim. (Leningrad)*, 1967, **40**, 342.
48. V. V. Volkhin, S. A. Kolesova and A. F. Kalashnikova, *Redk. Shchelochnye Elem., Sb. Dokl. Vses. Soveshch., 2nd, Novosibirsk* 1964 (Pub. 1967), p. 174.
49. V. V. Volkhin, S. A. Kolesova, E. A. Koshcheeva and T. P. Zatonskaya, *Tr. Nauch.-Issled. Inst. Khromatogr. Voronezh. Univ.*, 1968, 175.
50. E. A. Koshcheeva and V. V. Volkhin, *Zh. Neorgan. Khim.*, 1967, **12**, 2760.
51. S. A. Kolesova and V. V. Volkhin, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1966, **2**, 1110.
52. V. V. Volkhin and S. A. Kolesova, *Zh. Fiz. Khim.*, 1969, **43**, 1834.
53. W. E. Prot, E. R. Russell and H. J. Groh, Jr., *U.S. Patent*, 3,296,123 (1967).
54. B. Gorenc and L. Kosta, *Z. Anal. Chem.*, 1966, **223**, 410.
55. J. Schneider, *Thesis*, Technical University, West Berlin (1968).
56. S. Kawamura, H. Kuraku and K. Kurotaki, *Anal. Chim. Acta*, 1970, **49**, 317.
57. S. Kawamura, K. Kurotaki and M. Izawa, *Bull. Chem. Soc. Japan*, 1969, **42**, 3003.
58. V. Kouřím and B. Million, *Collection Czech. Chem. Commun.*, 1965, **30**, 2848.
59. D. van Deyck and L. H. Baetslé, *U.S. At. Energy Comm. Accession No.* 18564, *Rept. No.* EUR-2748e (1965).
60. D. Huys and L. H. Baetslé, *J. Inorg. Nucl. Chem.*, 1965 **27**, 2459.
61. V. Kouřím, J. Rais and J. Stejskal, *ibid.*, 1964, **26**, 1761.
62. J. Krtil, *J. Chromatog.*, 1965, **20**, 384.
63. S. Kawamura and K. Kurotaki, *ibid.*, 1969, **45**, 331.
64. J. Bastian and K. H. Lieser, *J. Inorg. Nucl. Chem.*, 1967, **29**, 827.
65. J. Krtil, *Radiochim. Acta*, 1967, **7**, 30.
66. R. B. Hahn and H. C. Klein, *Anal. Chem.*, 1968, **40**, 1135.
67. J. Krtil, *J. Inorg. Nucl. Chem.*, 1965, **27**, 1862.
68. J. Rais and V. Kouřím, *Czech. Patent* 117,268 (1966).
69. S. Kawamura, K. Kurotaki, H. Kuraku and M. Izawa, *J. Chromatog.*, 1967, **26**, 557.
70. J. Scheidhauer, G. Vergnaud and A. Flamant, *Commis. Energ. At. France, Rap.*, No. CEA-R-3585 (1968).
71. T. R. Folsom and R. Grismore, *IEEE Trans. Nucl. Sci.*, 1970, **17**, 202.
72. H. G. Petrow and H. Levine, *Anal. Chem.*, 1967, **39**, 360.
73. G. Branca, *Acqua Ind.*, 1964, **7**, 19.
74. H. Bernhard and K. H. Lieser, *Radiochim. Acta*, 1969, **11**, 153.
75. J. Krtil, *J. Chromatog.*, 1966, **21**, 85.
76. J. Krtil and J. Mencl, *Nuclear Res. Inst., Czech. Acad. Sci., Rept.* No. UJV 2242-Ch (1969).
77. J. Krtil, *J. Radioanal. Chem.*, 1968, **1**, 201.
78. Ch. Friedmann and T. Schönfeld, *Radiochem. Radioanal. Lett.*, 1969, **2**, 333.
79. B. M. Davis and F. Sebba, *J. Appl. Chem. (London)*, 1967, **17**, 40.
80. K. K. Panday and V. K. Agrawal, *J. Indian Chem. Soc.*, 1968, **45**, 984.
81. K. K. Panday and V. K. Agrawal, *Labdev*, 1970, **8A**, 152.
82. V. I. Baranovskii, Ya. Viza, G. S. Katykhin and M. K. Nikitin, *Radiokhimiya*, 1967, **9**, 698.
83. I. F. Karpova and E. V. Kazakov, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1966, **21**, 159.
84. N. Mishiro, A. Kamoshida, S. Kadoya and T. Ishihara, *Nippon Genshiryoku Gakkaishi*, 1964, **6**, 2.
85. K. Terada, H. Hayakawa, K. Sawada and T. Kiba, *Talanta*, 1970, **17**, 955.
86. V. V. Volkhin, B. I. Lvovich, S. A. Kolesova, G. V. Leonteva, A. F. Kalashnikova, Yu. I. Nalimov and A. G. Kubareva, *Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met.*, 1966, **9**, 28.
87. J. Soukup, J. Doležal, V. Kouřím and J. Stejskal, *Czech. Patent Appl.* PV 1268 (1968).
88. I. F. Karpova and E. V. Kazakov, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1967, **22**, 136.
89. E. V. Kazakov and I. F. Karpova, *ibid.*, 1967, **22**, 151.
90. E. V. Kazakov and I. F. Karpova, *ibid.*, 1968, **23**, 105.
91. K. Watari, K. Imai and M. Izawa, *J. Nucl. Sci. Technol. (Tokyo)*, 1967, **4**, 190.
92. *Netherlands, Patent Application*, 6,412,980 (1965).
93. K. Watari, K. Imai and M. Izawa, *J. Nucl. Sci. Technol. (Tokyo)* 1968, **5**, 309.
94. *Idem*, *ibid.*, 1969, **6**, 522.
95. E. V. Kazakov, A. V. Markovich, K. K. Kalninsh and I. F. Karpova, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1970, **25**, 123.
96. A. Bonnin and P. Poirier, *French Patent*, 1,480,148 (1967).
97. I. V. Tananaev and A. P. Korolkov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1965, **1**, 100.
98. A S. Kozlov and Yu. Mizhidiin, *Red. Shchelochnye Elem., Sb. Dokl. Vses. Soveshch., 2nd, Novosibirsk* 1964 (Pub. 1967), p. 300.

99. I. V. Tananaev and A. P. Korolkov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1965, **1**, 607.
100. E. V. Kazakov and I. F. Karpova, *Vestn. Leningrad. Univ., Ser. Fiz. Khim.*, 1966, **21**, 141.
101. I. V. Tananaev and A. P. Korolkov, *Izv. Akad. Nauk SSSR, Neorgan. Mater.*, 1965, **1**, 1577.
102. V. V. Volkhin and E. A. Kosheeva, *ibid.*, 1968, **4**, 914.
103. V. G. Kuznetsov, Z. V. Popova and G. B. Seifer, *Zh. Neorgan. Khim.*, 1970, **15**, 2710.
104. H. Ti Tien, *J. Colloid Interface Sci.*, 1966, **21**, 94.
105. P. Cloos, A. Herbillon and J. Echeverria, *Trans., Intern. Congr. Soil Sci.*, 9th, 1968, **2**, 733
106. K. K. Hojun Kogya, *German Patent*, 1,223,816 (1966).
107. W. T. Granquist and S. S. Pollack, *Am. Mineral.*, 1967, **52**, 212.
108. R. M. Barrer, *Endeavour*, 1964, 122.
109. *Idem, Ber. Bunsenges. Physik. Chem.*, 1965, **69**, 786.
110. *Idem, Proc. Brit. Ceram. Soc.*, 1964, 145.
111. *Idem, Chem. in Brit.*, 1966, 380.
112. H. S. Sherry, in *Ion Exchange, Vol. 2*, (J. A. Marinsky, ed.), pp. 89–133. Dekker, New York, 1969.
113. D. W. Breck, *J. Chem. Educ.*, 1964, **41**, 678.
114. J. Turkevich, *Catalysis Rev.*, 1967 **1**, 1.
115. F. Wolf, H. Fuertig and U. Haedicke, *Chem. Tech. (Berlin)*, 1966, **18**, 524.
116. K. F. Fischer and W. M. Meier, *Fortschr. Mineral.*, 1964, **42**, 50.
117. Ch. Kato, *Kagaku To Kogyo (Tokyo)*, 1968, **21**, 1251.
118. *Sbornik Sintez, Issledovanyie i Primeneniye Zoelitov*, Nauka, Moscow, 1965.
119. Ch. M. Minachev, V. I. Garanin and Ya. I. Isakov, *Usp. Khim.*, 1966, **35**, 2151.
120. R. J. Argauer, *U.S. Patent*, 3,431,219 (1969).
121. D. W. Breck and E. M. Flanigen, *Mol. Sieves, Pap. Conf.* 1967 (Pub. 1968), p. 47, Soc. Chem. Ind., London.
122. S. P. Zhdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 950.
123. J. Ciric, *Science*, 1967, **155**, 689.
124. Ya. V. Mirskii, M. G. Mitrofanov, B. M. Papkov, L. I. Bolotov and L. F. Ruchko, *USSR Patent*, 170,912 (1965).
125. G. V. Tsitsishvili and T. A. Gedzhadze, *Rentgenogr. Mineraln. Syrya, Min. Geol. i Okhrany Nedr. SSSR, Vses. Nauch.-Issled. Inst. Mineraln. Syrya, Akad. Nauk SSSR*, 1964, p. 113.
126. Ya. V. Mirskii, A. Z. Dorogochinskii, I. L. Aleksandrova, V. G. Golovko and L. F. Ruchko, *Tr. Grozn. Neft. Nauch.-Issled. Inst.*, 1967, No. 23, 205.
127. *Netherlands, Patent Application*, 6,503,538 (1965).
128. H. Gaus and E. Hoinkis, *Z. Naturforsch.*, 1969, **24a**, 1511.
129. *Netherland Patent Application* 298,716 (1965).
130. F. Polak and J. Wilkosz, *Zesz. Nauk. Univ. Jagiellon, Pr. Chem.*, 1969, No. 14, 185.
131. S. P. Zhdanov, N. N. Samulevich and E. N. Egorova, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 129.
132. M. E. Ovsepyan and C. P. Zhdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 11.
133. J. M. Vergnaud, M. Mange, M. Guyot de la Hardrouyere and B. Ray-Coquais, *Bull. Soc. Chim. France*, 1965, 1279.
134. Ya. V. Mirskii and M. G. Mitrofanov, *USSR Patent*, 146,285 (1968).
135. V. N. Mazin, *USSR Patent*, 172,721 (1965).
136. G. H. Kuehl, *Mol. Sieves, Pap. Conf.*, 1967 (Pub. 1968), p. 85. Soc. Chem. Ind., London.
137. V. M. Lukyanovich, E. I. Evko and V. V. Churakov, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 121.
138. *Netherlands, Patent Application*, 6,504,679 (1965).
139. H. S. Sherry, *J. Phys. Chem.* 1966, **70**, 1158.
140. L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, 1960, **82**, 1041.
141. E. Dempsey, G. H. Kuehl and D. H. Olson, *J. Phys. Chem.*, 1969, **73**, 387.
142. R. L. Mays, P. E. Pickert, A. P. Bolton and M. A. Lanewala, *Oil and Gas J.*, 1965, **63**, 91.
143. G. T. Kerr, *J. Phys. Chem.*, 1968, **72**, 2594.
144. *Idem, ibid*, 1969, **73**, 2780.
145. D. Barthomeuf and R. Beaumont, *Compt. Rend.*, 1969, **269C**, 1345.
146. G. T. Kerr, *Inorg. Chem.*, 1966, **5**, 1537.
147. W. M. Meier and G. T. Kokotailo, *Z. Krist.*, 1965, **121**, 211.
148. W. H. Baur, *Am. Mineralogist*, 1964, **49**, 697.
149. A. Knappwost, W. Gunsser and H. Lechert, *Z. Naturforsch.*, 1966, **21a**, 1200.
150. A. Knappwost, H. Lechert and W. Gunsser, *Z. Phys. Chem. (Frankfurt)*, 1968, **58**, 278.
151. H. Lechert, W. Gunsser and A. Knappwost, *Ber. Bunsenges. Phys. Chem.*, 1968, **72**, 84.
152. D. H. Olson, *J. Phys. Chem.*, 1970, **74**, 2758.

153. E. Dempsey, *ibid.*, 1969, **73**, 3660.
154. H. S. Sherry and H. F. Walton, *ibid.*, 1967, **71**, 1457.
155. P. Collin and R. Wey, *Compt. Rend.*, 1970, **270D**, 1069.
156. V. A. Silchenko, N. N. Pafomov, I. V. Matyash and M. A. Piontkovskaya, *Dopov. Akad. Nauk Ukr. RSR Ser. A*, 1970, **32**, 235.
157. T. I. Barry and L. A. Lay, *J. Phys. Chem. Solids*, 1966, **27**, 1821.
158. T. I. Barry and L. A. Lay, *Nature*, 1965, **208**, 1312.
159. I. V. Matyash, V. V. Mank, Ya. Ya. Sbcherbak, M. A. Piontkovskaya and R. S. Tyutyunnik, *Zh. Neorgan. Khim.*, 1969, **14**, 508.
160. W. N. Delgass, R. L. Garten and M. Boudart, *J. Phys. Chem.*, 1969, **73**, 2970.
161. W. N. Delgass, R. L. Garten and M. Boudart, *J. Chem. Phys.*, 1969, **50**, 4603.
162. V. I. Goldanskii, I. I. Suzdalev, A. S. Plachinda and L. G. Shtyrkov, *Dokl. Akad. Nauk SSSR*, 1966, **169**, 872.
163. J. A. Morice and L. V. C. Rees, *Trans. Faraday Soc.*, 1968, **64**, 1388.
164. T. I. Barry and L. A. Lay, *J. Phys. Chem. Solids*, 1968, **29**, 1395.
165. E. Dempsey and D. H. Olson, *J. Phys. Chem.*, 1970, **74**, 305.
166. A. Dyer and J. M. Fawcett, *J. Inorg. Nucl. Chem.*, 1966, **28**, 615.
167. K. Seff and D. P. Shoemaker, *Acta Cryst.*, 1967, **22**, 162.
168. C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, 1966, **70**, 1413.
169. J. W. Ward and H. W. Hagbood, *ibid.*, 1966, **70**, 1178.
170. D. H. Olson, *J. Phys. Chem.*, 1968, **72**, 4366.
171. J. M. Bennett and J. V. Smith, *Mater. Res. Bull.*, 1968, **3**, 933.
172. *Idem*, *ibid.*, 1968, **3**, 865.
173. *Idem*, *ibid.*, 1968, **3**, 633.
174. *Idem*, *ibid.*, 1969, **4**, 7.
175. *Idem*, *ibid.*, 1969, **4**, 77.
176. *Idem*, *ibid.*, 1969, **4**, 343.
177. J. T. Richardson, *J. Catal.*, 1967, **9**, 178.
178. J. W. Ward, *J. Phys. Chem.*, 1970, **74**, 3021.
179. J. V. Smith, J. M. Bennett and E. M. Flanigen, *Nature*, 1967, **215**, 241.
180. G. R. Eulenberger, J. G. Keil and D. P. Shoemaker, *J. Phys. Chem.*, 1967, **71**, 1812.
181. J. V. Smith and L. G. Dowell, *Z. Kristallogr.*, 1967, **126**, 135.
182. L. Moscou and M. Lakeman, *J. Catal.*, 1970, **16**, 173.
183. D. H. Olson, G. T. Kokotailo and J. F. Charnell, *J. Colloid Interface Sci.*, 1968, **28**, 305.
184. P. E. Pickert, J. A. Rabo, E. Dempsey and V. Schomaker, *Proc. 3rd Intern. Congr. Catalysis, Amsterdam*, 1965, **1**, 714.
185. D. H. Olson, G. T. Kokotailo and J. F. Charnell, *Nature*, 1967, **215**, 270.
186. R. M. Barrer and A. J. Walker, *Trans. Faraday Soc.*, 1964, **60**, 171.
187. D. Kunath, H. J. Spangenberg, H. Stach and W. Shirmer, *Z. Chem.*, 1970, **10**, 1.
188. R. Schoonheydt and J. B. Uytterhoeven, *Clay Miner.*, 1969, **8**, 71.
189. C. L. Angell and P. C. Schaffer, *J. Phys. Chem.*, 1965, **69**, 3463.
190. Yu. S. Khodakov, I. D. Mikheikin, V. S. Nakhshunov, V. A. Shvets, V. B. Kazanskii and K. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 523.
191. J. L. Carter, P. J. Lucchesi and D. J. C. Yates, *J. Phys. Chem.*, 1964, **68**, 1385.
192. H. W. Hagbood, *ibid.*, 1965, **69**, 1764.
193. Y. Watanabe and H. W. Hagbood, *ibid.*, 1968, **72**, 3066.
194. D. H. Olson, *ibid.*, 1968, **72**, 1400.
195. J. W. Ward, *J. Catal.*, 1968, **11**, 238.
196. J. W. Ward, *J. Phys. Chem.*, 1968, **72**, 4211.
197. J. W. Ward, *J. Catal.*, 1968, **10**, 34.
198. J. W. Ward, *J. Phys. Chem.*, 1968, **72**, 2689.
199. P. E. Eberly, *ibid.*, 1968, **72**, 1042.
200. J. B. Uytterhoeven, R. Schoonheydt, B. V. Liengme and W. K. Hall, *J. Catal.*, 1969, **13**, 425 425.
201. L. V. Pansevich-Kolyada and V. N. Sharai, *Vestsi Akad. Navuk Belorus. SSR, Ser. Khim. Navuk*, 85 (1970).
202. W. J. Mattox, *U.S. Patent* 3,405,074 (1968).
203. V. Ya. Nikolina and Ė. B. Ledeneva, *USSR Patent* 172,280 (1965).
204. G. T. Kerr, *U. S. Patent* 3,228,969 (1966).
205. E. B. Cornelius, J. E. McEvoy and G. A. Mills, *U.S. Patent* 3,365,272 (1968).
206. S. A. Levina, L. N. Malashevich and N. F. Ermolenko, *Vestsi Akad. Navuk Belorusk. SSR, Ser. Khim. Navuk*, 1965, 10.

207. W. J. Mattox and E. M. Gladrow, *U.S. Patent* 3,369,865 (1968).
208. A. M. Tolmachev, T. V. Zotov, V. A. Fedorov and Ya. V. Mirskii, *Zh. Fiz. Khim.*, 1966, **40**, 2598.
209. H. Fuertig and F. Wolf, *Tonind. Ztg. Keram. Rundschau*, 1966, **90**, 303.
210. L. L. Ames Jr., *Can. Mineralogist*, 1966, **8**, 515.
211. I. E. Neimark, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 959.
212. M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, 1964, **159**, 166.
213. F. Wolf and U. Haedicke, *Tonind. Ztg. Keram. Rundschau*, 1967, **91**, 45.
214. *French Patent*, 1,463,445 (1966).
215. K. Tsutsumi and H. Takahashi, *J. Phys. Chem.*, 1970, **74**, 2710.
216. F. Wolf and U. Haedicke, *Tonind. Ztg. Keram. Rundschau*, 1967, **91**, 48.
217. D. J. C. Yates, *J. Phys. Chem.*, 1965, **69**, 1676.
218. V. S. Vinogradova, L. S. Kofman, B. A. Lipkind, L. M. Medvedeva and A. T. Slepneva, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 285.
219. L. G. Christner, B. V. Liengme and W. K. Hall, *Trans. Faraday Soc.*, 1968, **64**, 1679.
220. A. S. Berger and L. K. Yakovlev, *Zh. Prikl. Khim. (Leningrad)*, 1965, **38**, 1240.
221. Yu. S. Khodakov, V. S. Nakhshunov and K. M. Minachev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 1699.
222. M. Nakagaki and T. Fujie, *Yakugaku Zasshi*, 1968, **88**, 1545.
223. H. Thibon and N. Bressange, *Bull. Soc. Chim. France*, 1967, 3614.
224. L. V. C. Rees and C. J. Williams, *Trans. Faraday Soc.*, 1965, **61**, 1481.
225. J. A. Rabo, C. L. Angell, P. H. Kasai and V. Schomaker, *Discussions Faraday Soc.*, 1966, 328.
226. *Netherland Application*, 6,503,431 (1965).
227. G. V. Tsitsishvili, T. G. Andronikashvili, T. A. Chumburidze and S. S. Chkheidze, *Zh. Fiz. Khim.*, 1969, **43**, 2670.
228. S. A. Levina, L. N. Malashevich, N. F. Ermolenko and A. A. Prokopovich, *Kolloidn. Zh.*, 1967, **29**, 219.
229. A. I. Rastrenenko, S. N. Antonovskaya and I. E. Neimark, *ibid.*, 1965, **27**, 269.
230. V. Bosáček, *Dokl. Akad. Nauk SSSR*, 1966, **168**, 126.
231. S. P. Zhdanov, V. N. Novikova, L. F. Pavlova and Yu. A. Eltekov, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 178.
232. P. Collin and R. Wey, *Compt. Rend.*, 1970, **270D**, 457.
233. E. M. Eremenko, M. A. Piontkovskaya, I. V. Matyash, V. V. Mank, M. G. Starkov and I. E. Neimark, *Zh. Strukt. Khim.*, 1966, **7**, 106.
234. M. Mange, J. L. Thomas and Ch. Eyraud, *Bull. Soc. Chim. France*, 1969, 3375.
235. I. E. Neimark, *Izv. Otd. Khim. Nauki, Bulg. Akad. Nauk*, 1968, **1**, 31.
236. M. M. Dubinin, O. Kadlec and A. Zukal, *Collection Czech. Chem. Commun.*, 1966, **31**, 406.
237. M. M. Dubinin, Yu. F. Berezkina, E. F. Polstyanov, Z. A. Ryabikova and A. I. Sarakhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1731.
238. B. Morris, *J. Colloid Interface Sci.*, 1968, **28**, 149.
239. A. M. Tolmachev and V. A. Fedorov, *Vestn. Mosk. Univ., Ser. II*, 1966, **21**, 32.
240. G. V. Tsitsishvili, T. G. Andronikashvili and T. A. Chumburidze, *Dokl. Akad. Nauk SSSR*, 1966, **170**, 611.
241. G. V. Tsitsishvili, T. G. Andronikashvili and T. A. Shumburidze, *ibid.*, 1965, **164**, 1104.
242. B. V. Romanovskii, K. Tchoang, K. V. Topcieva and L. I. Piguzova, *Kinetika i Kataliz*, 1966, **7**, 841.
243. G. D. Bagratishvili, G. V. Tsitsishvili, M. L. Kantariya and N. I. Oniashvili, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 65.
244. D. A. Young, *U.S. Patent* 3,460,904 (1969).
245. J. W. Ward, *J. Phys. Chem.*, 1969, **73**, 2086.
246. D. A. Young, *U.S. Patent* 3,383,169 (1968).
247. V. G. Ilin, I. E. Neimark and A. I. Rastrenenko, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 185.
248. A. P. Bolton and R. L. Mays, *Chim. Ind. (Milan)*, 1970, **52**, 121.
249. G. T. Kerr, *J. Catal.*, 1969, **15**, 200.
250. J. W. Ward, *ibid.*, 1967, **9**, 225.
251. J. Uytterhoeven, L. G. Christner and W. K. Hall, *J. Phys. Chem.*, 1965, **69**, 2117.
252. B. V. Liengme and W. K. Hall, *Trans. Faraday Soc.*, 1966, **62**, 3229.
253. J. W. Ward and R. C. Hansford, *J. Catal.*, 1969, **13**, 364.
254. S. P. Zhdanov, V. I. Lygin and T. I. Titova, *Materialy Vses. Soveshch. po Tseolitam, 2nd, Leningrad* 1964 (Pub. 1965), p. 53.
255. N. W. Cant and W. K. Hall, *Trans. Faraday Soc.*, 1968, **64**, 1093.

256. J. L. White, A. W. Jelli, J. M. Andre and J. J. Fripiat, *ibid.*, 1967, **63**, 461.
257. S. P. Zhdanov, A. V. Kiselev, V. I. Lygin and T. I. Titova, *Zh. Fiz. Khim.*, 1966, **40**, 1041.
258. S. P. Zhdanov, A. V. Kiselev, V. I. Lygin, M. E. Ovespyan and T. I. Titova, *ibid.*, 1965, **39**, 2454.
259. T. R. Hughes and H. M. White, *J. Phys. Chem.*, 1967, **71**, 2192.
260. P. E. Eberly, Jr., *ibid.*, 1967, **71**, 1717.
261. J. W. Ward, *J. Catal.*, 1967, **9**, 396.
262. *Idem, ibid.*, 1968, **11**, 251.
263. J. G. Larson, H. R. Gerberich and W. K. Hall, *J. Am. Chem. Soc.*, 1965, **87**, 1880.
264. J. W. Ward, *J. Phys. Chem.*, 1967, **71**, 3106.
265. J. B. Uytterhoeven, P. Jacobs, M. Markay and R. Schoonheydt, *ibid.*, 1968, **72**, 1768.
266. D. H. Olson and E. Dempsey, *J. Catal.*, 1969, **13**, 221.
267. E. Dempsey, *Mol. Sieves, Pap. Conf.* 1967 (Pub. 1968), p. 293. Soc. Chem. Ind., London.
268. J. V. Smith and J. M. Bennett, *Nature*, 1968, **219**, 1040.
269. V. G. Gvakhariya, V. I. Kvlividze, A. A. Kubasov, B. V. Romanovskii, K. V. Topchievea and G. V. Tsitsishvili, *Kinetika i Kataliz*, 1969, **10**, 1392.
270. G. T. Kerr, *J. Phys. Chem.*, 1967, **71**, 4155.
271. G. T. Kerr and G. F. Shipman, *ibid.*, 1968, **72**, 3071.
272. C. V. McDaniel and P. K. Maher, *Mol. Sieves, Pap. Conf.* 1967 (Pub. 1968), p. 186. Soc. Chem. Ind., London.
273. R. M. Barrer, J. A. Davies and L. V. C. Rees, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2599.
274. *Idem, ibid.*, 1968, **30**, 3333.
275. M. Cruceanu and M. Dima, *An. Stiint Univ. "Al. I. Cuza" Iasi, Sect. I.C.*, 1966, **12**, 207.
276. R. M. Barrer, L. V. C. Rees and M. Shamsuzzuha, *J. Inorg. Nucl. Chem.*, 1966, **28**, 629.
277. A. M. Tolmachev and V. A. Fedorov, *Zh. Fiz. Khim.*, 1965, **39**, 2259.
278. L. L. Ames, Jr., *Am. Mineralogist*, 1964, **49**, 127.
279. E. Vansant, B. K. G. Theng, A. Maes and J. B. Uytterhoeven, *Bull. Groupe Fr. Argiles*, 1969, **21**, 46.
280. B. K. G. Theng, E. Vansant and J. B. Uytterhoeven, *Trans. Faraday Soc.*, 1968, **64**, 3370.
281. F. A. Belinskaya, S. P. Zhdanov, E. A. Materova and M. A. Shubaeva, *Teor. Ionnogo Obmena Khromatogr., Tr. Vses. Nauch.-Tekh. Konf.* 1965 (Pub. 1968), p. 37. Edited by V. V. Rachsinskii, Izd. Nauka, Moscow.
282. H. S. Sherry, *J. Phys. Chem.*, 1968, **72**, 4086.
283. *Idem, ibid.*, 1967, **71**, 780.
284. A. Dyer and R. B. Gettins, *Proc. Soc. Chem. Ind. Conf. Ion-Exchange in Process Industries*, London (1969), p. 357.
285. R. Russu, *Rev. Chim. (Bucharest)*, 1969, **20**, 745.
286. J. F. Harvey, J. P. Redfern and J. E. Salmon, *Trans. Faraday Soc.*, 1966, **62**, 198.
287. M. Cruceanu, M. Dima and F. Gothard, *An. Stiint Univ. "Al. I. Cuza" Iasi, Sect. IC Chim.*, 1966, **12**, 201.
288. D. H. Olson and H. S. Sherry, *J. Phys. Chem.*, 1968, **72**, 4095.
289. H. S. Sherry, *J. Colloid Interface Sci.*, 1968, **28**, 288.
290. L. L. Ames, Jr., *J. Inorg. Nucl. Chem.*, 1965, **27**, 885.
291. R. M. Barrer, L. V. C. Rees and D. J. Ward, *Proc. Roy. Soc.*, 1963, **A273**, 180.
292. A. M. Tolmachev, V. A. Fedorov and G. M. Panchenkov, *Issled. Svoistv Ionoobmen. Materialov Akad. Nauk SSSR, Inst. Fiz. Khim.*, 1964, 88.
293. A. M. Tolmachev and V. A. Fedorov, *Vestn. Mosk. Univ., Ser. II.* 1966, **21**, 34.
294. A. M. Kuznetsov and V. A. Kuznetsov, *Zh. Prikl. Khim. (Leningrad)*, 1968, **41**, 2183.
295. M. V. Šušić, V. M. Radak, N. A. Petranović and D. S. Veselinović, *Trans. Faraday Soc.*, 1966, **62**, 3479.
296. A. Dyer, R. B. Gettins and A. Molyneux, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2823.
297. L. L. Ames, *Can. Mineralogist*, 1965, **8**, 325.
298. F. Wolf and H. Fuertig, *Kolloid-Z. Z. Polymere*, 1965, **206**, 48.
299. F. Wolf and H. Fuertig, *Chem. Tech. (Berlin)*, 1966, **18**, 1.
300. H. S. Sherry, *J. Phys. Chem.*, 1966, **70**, 1332.
301. P. D. Radovan, O. M. Gacinović and I. J. Gal, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2981.
302. F. Wolf and U. Haedicke, *Tonind. Ztg. Keram. Rundschau*, 1967, **91**, 41.
303. L. L. Ames, Jr., *Am. Mineralogist*, 1965, **50**, 465.
304. A. Dyer, R. B. Gettins and J. G. Brown, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2389.
305. E. Hoinkis and H. W. Levi, *Z. Naturforsch.*, 1967, **22a**, 226.
306. *Idem, Proc. Soc. Chem. Ind. Conf. Ion-Exchange in Process Industries*, London 1969, p. 339.
307. C. Paravano, J. D. Baldeschwieler and M. Boudart, *Science*, 1967, **155**, 1535.
308. A. Dyer and R. B. Gettins, *J. Inorg. Nucl. Chem.*, 1970, **32**, 319.

309. A. Dyer, R. B. Gettins and R. P. Townsend, *ibid.*, 1970, **32**, 2395.
310. E. Hoinkis and H. W. Levi, *Z. Naturforsch.*, 1969, **24a**, 1784.
311. *Idem*, *ibid.*, 1969, **24a**, 1672.
312. *Idem*, *ibid.*, 1968, **23a**, 813.
313. A. Dyer and R. B. Gettins, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2401.
314. P. C. Huang, A. Mizany and J. L. Pavley, *J. Phys. Chem.*, 1964, **68**, 2575.
315. *Netherlands, Patent Application*, 298,606 (1965).
316. D. B. Hawkins, *Mater. Res. Bull.*, 1967, **2**, 951.
317. L. L. Ames, Jr., *Am. Mineralogist*, 1963, **48**, 1374.
318. L. B. Sand, *U.S. Patent* 3,436,174 (1969).
319. I. M. Belenkaya, M. M. Dubinin and I. I. Krishtofori, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2164.
320. M. M. Dubinin, E. G. Zhukovskaya, V. M. Lukyanovich, K. O. Mordmaa, E. F. Polsyanov and E. E. Senderov, *ibid.*, 1965, 1500.
321. D. B. Hawkins, *Mater. Res. Bull.*, 1967, **2**, 1021.
322. K. Ryoichi, *Kobutsugaku Zasshi*, 1964, **7**, 39.
323. N. Waitsu, *ibid.*, 1964, **7**, 23.
324. L. L. Ames, Jr., *J. Inorg. Nucl. Chem.*, 1967, **29**, 262.
325. R. M. Barrer, R. Papadopoulos and L. V. C. Rees, *ibid.*, 1967, **29**, 2047.
326. B. M. Moiseev, *Byul., Nauch.-Tekh., Inform. Min. Geol. SSSR, Ser. Izuch. Veshchestv. Sostava Miner. Syrya Tekhnol. Obogashch. Rud.* 1967, No. 5, p. 18.
327. L. L. Ames, Jr., *Am. Mineralogist*, 1964, **49**, 1099.
328. R. M. Barrer and J. A. Lee, *J. Colloid Interface Sci.*, 1969, **30**, 111.
329. R. M. Barrer and D. J. Marshall, *Am. Mineralogist*, 1965, **50**, 484.
330. J. V. Smith, C. R. Knowles and F. Rinaldi, *Acta Crystallog.*, 1964, **17**, 374.
331. G. T. Kerr, *U.S. Patent*, 3,459,676 (1969).
332. L. P. Shirinskaya, N. F. Ermolenko, V. Ya. Nikolina, Yu. G. Zonov and T. G. Ulasik, *Dokl. Akad. Nauk Beloruss. SSR*, 1966, **10**, 961.
333. H. S. Sherry, *Proc. Soc. Chem. Ind. Conf. Ion-Exchange in Process Industries*, London 1969, p. 328.
334. L. I. Piguzova, V. Ya. Nikolina, M. M. Dubinin and T. N. Shishakova, *Khim. i Tekhnol. Topliv i Masel*, 1965, **10**, 32.
335. M. M. Dubinin, V. Ya. Nikolina, L. I. Ciguzova and T. N. Shishakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1116.
336. S. P. Zhdanov and B. G. Novikov, *Dokl. Akad. Nauk SSSR*, 1966, **166**, 1107.
337. Ya. I. Ryskin, S. P. Zhdanov, N. A. Mitropolskii, I. V. Gessen, G. P. Stavitskaya and M. A. Shubaeva, *Teor. Eksp. Khim.*, 1967, **3**, 324.
338. O. A. Glonti and N. A. Shishakov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1275.
339. R. M. Barrer, J. A. Davies and L. V. C. Rees, *J. Inorg. Nucl. Chem.*, 1969, **31**, 219.
340. L. L. Ames and B. W. Mercer, *U.S. At. Energy Comm. Rept.*, BNWL-732 (1968).
341. A. Dyer and A. Molyneux, *J. Inorg. Nucl. Chem.*, 1968, **30**, 829.
342. W. D. Balgord, *Thesis*, Pensylvania State Univ.; *Univ. Microfilms* (*Ann. Arbor, Mich.*), Order No. 67-11,178; *Diss. Abstr.*, 1967, **B28**, 1103.
343. L. L. Ames, *Am. Mineralogist*, 1966, **51**, 903.
344. C. De Kimpe, *Clay Miner.*, 1967, **7**, 203.
345. G. T. Kerr, *J. Phys. Chem.*, 1968, **72**, 1385.
346. A. M. Taylor and R. Roy, *Am. Mineralogist*, 1964, **49**, 656.
347. T. N. Shishakova and M. M. Dubinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1965, 1303.
348. J. L. Guth, *Rev. Chim. Minerale*, 1965, **2**, 127.
349. W. R. Grace & Co., *Brit. Patent*,1,010,402 (1965).
350. W. L. Haden, Jr., *U.S. At. Energy Comm.* No. 35502, *Rept.* NYO-2911-1 (1964).
351. D. A. Young, *Brit. Patent*, 1,188,188 (1970).
352. V. I. Karzhev, L. I. Piguzova, N. V. Goncharova, V. P. Svirina, N. V. Krivozubova, G. L. Goikhman, E. A. Bulekova and A. S. Vitukhina, *USSR Patent* 265,078 (1970).
353. E. Lamb, *Nucl. Sci. Eng.*, 1966, **24**, 118.
354. R. E. Lewis, T. A. Butler and E. Lamb, *U.S. At. Energy Comm. Rept.*, ORNL 3765 (1965).
355. B. W. Mercer, L. L. Ames and C. J. Tonhill, *Am. Chem. Soc., Div. Water, Air Waste Chem., Gen. Pap.*, 1968, **8**, 97.
356. C. V. McDaniel and P. K. Maher, *French Patent*, 1,542,754 (1968).
357. V. N. Shchebetkovskii, *Radiokhimiya*, 1968, **10**, 151.
358. O. M. Gacinović, P. D. Radovanov and I. J. Gal, *Isotopenpraxis*, 1969, **5**, 420.
359. M. V. Šušić and V. M. Radak, *Bull. Boris Kidrich Inst. Nucl. Sci.*, 1966, **17**, 243.

360. U. Kuhlmann, *French Patent*, 1,560,332 (1969).
361. D. C. Freeman, *U.S. Patent*, 3,186,875 (1965).
362. R. P. Crowley, *U.S. Patent*, 3,266,973 (1966).
363. R. Caramazza, V. Elia and E. Drioli, *Corsi Semin. Chim.* 1968, 50.
364. A. M. Kuznetsov and V. A. Kuznetsov, *Zh. Neorgan. Khim.*, 1968, **13**, 237.
365. A. M. Tolmachev, V. A. Fedorov, G. M. Panchenkov and N. N. Zveva, *Zh. Fiz. Khim.*, 1965, **39**, 1780.
366. G. L. Ribaud, *French Patent*, 1,385,071 (1965).
367. G. T. Kerr, *J. Phys. Chem.*, 1966, **70**, 1047.
368. J. R. Ciric and J. Luther, *U.S. Patent*, 3,433,589 (1969).
369. H. Fuertig and F. Wolf, *Tonind. Ztg. Keram. Rundschau*, 1966, **90**, 297.
370. G. Montel, *Bull. Soc. Chim. France*, 1968, 1693.
371. J. C. Elliott and R. A. Young, *Nature*, 1967, **214**, 904.
372. G. Montel, *Ann. Chim. (Paris)*, 1969, **4**, 255.
373. Ch. Y. C. Pak and F. C. Bartter, *Biochim. Biophys. Acta*, 1967, **141**, 401.
374. *Idem*, *ibid.*, 1967, **141**, 410.
375. F. Samec and G. Montel, *Compt. Rend*, 1966, **262C**, 918.
376. G. Wright and G. Montel, *ibid.*, 1969, **268C**, 2169.
377. F. Samec and G. Montel, *ibid.*, 1966, **262C**, 837.
378. G. Wright, *Ann. Chim. (Paris)*, 1970, **5**, 39.
379. A. Knappwost and U. Lepper, *Z. Naturforsch.*, 1967, **22a**, 975.
380. T. S. B. Narasaraju, R. P. Singh and V. L. N. Rao, *Indian J. Chem.*, 1970, **8**, 296.
381. G. S. Ingram, *Bull. Soc. Chim. France*, 1968, 1841.
382. V. A. Tyagai, N. A. Petrova and R. L. Treskunova, *Elektrokhimiya*, 1968, **4**, 179.
383. N. F. Chelishchev, *Dokl. Akad. Nauk SSSR*, 1970, **192**, 1127.
384. B. I. Lvovich and V. V. Volkhin, *Zh. Neorgan. Khim.*, 1970, **15**, 520.
385. B. V. Eremenko, L. M. Sidlyar and E. T. Uskova, *Ionity Ionnyi Obmen, Akad. Nauk SSSR, Sb. Statei*, 1966, 76.
386. V. V. Volkhin and B. I. Lvovich, *Zh. Prikl. Khim. (Leningrad)* 1967, **40**, 988.
387. V. V. Volkhin and B. I. Lvovich, *Sin. Svoistva Ionoobmen. Mater.*, p. 73. Izd. Nauka, Moscow 1968.
388. H. O. Phillips and K. A. Kraus, *J. Chromatog.*, 1965, **17**, 549.
389. Z. Goerlich, *Zeszyty Nauk. Univ. Jagiel., Ser. Nauk. Chem.*, 1962, **7**, 5.
390. B. I. Lvovich and V. V. Volkhin, *Zh. Neorgan. Khim.*, 1968, **13**, 570.
391. C. W. Sill, *Health Physics*, 1969, **17**, 89.
392. L. Berák and J. Münich, *Collection Czech. Chem. Commun.*, 1966, **31**, 881.
393. *Idem*, *Nuclear Res. Inst., Czech. Acad. Sci, Rept.* No. 956/63 (1963).
394. L. L. Berák, *Collection Czech. Chem. Commun.*, 1965, **30**, 1490.
395. L. Berák and J. Münich, *Nuclear Res. Inst., Czech. Acad. Sci., Rept.* No. 1382/65 (1965).
396. L. Berák, J. Moravec and V. Šára, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2637.
397. L. Berák and J. Moravec, *Radiochem. Conf., Abstr. Pap., Bratislava* 1966, p. 18.
398. O. Vojtěch, J. Moravec, F. Volf and M. Dlouhá, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3725.
399. O. Vojtěch and J. Vachuška, *J. Thermal Analysis*, 1971, **3**, 35.
400. J. Moravec and O. Vojtěch, *Nuclear Res. Inst., Czech. Acad. Sci., Rept.*, No. 2395 (1970).
401. O. Vojtěch, *Nuclear Res. Inst., Czech. Acad. Sci.*, Report No. 2361 (1970).
402. J. Moravec and O. Vojtěch, *Radiochem. Radioanal. Lett.*, 1970, **4**, 271.
403. O. Vojtěch and J. Moravec, *Nuclear Res. Inst., Czech. Acad. Sci., Rept.* No. 2415 (1970).

Talanta, 1972, Vol. 19, pp. 1285 to 1293. Pergamon Press. Printed in Northern Ireland

A CONTRIBUTION TO THE PROBLEM OF INCREASING THE SENSITIVITY OF ANODIC-STRIPPING VOLTAMMETRY

LUDMILA HUDEROVÁ and KAREL ŠTULÍK®
Research Institute for Pharmacy and Biochemistry, and
Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia

(*Received* 18 *January* 1972. *Accepted* 3 *March* 1972)

Summary—A brief discussion of problems connected with increasing the sensitivity of anodic-stripping determinations is presented. A new microcell for anodic-stripping voltammetry in solution volumes down to about 0.01 ml was constructed. The effect of the solution volume, the mercury-drop electrode size, and of the pre-electrolysis time and potential on the sensitivity of determinations was studied and the reproducibility of results for determinations of lead in mineral acids is given. It was found that nanogram amounts of heavy metals can easily be determined in this way. In determination of 2 ng of Pb^{2+} in 0.02 ml of solution the results were 2.00 ± 0.13 ng (95% confidence limits), the mean relative deviation being 6.3%. For determination of copper in KNO_3, stripping microanalysis was compared with atomic-absorption spectrophotometry. Advantages and disadvantages of stripping voltammetry on the macro- and micro-scales are discussed.

TWO OF THE MOST IMPORTANT ASPECTS of anodic-stripping voltammetry, as with any other analytical technique, are its selectivity and sensitivity. The former was dealt with in our previous paper.[1] The problem of increasing the sensitivity is chiefly that of increasing the electrolytic current due to dissolution of the species monitored, compared to the background current value. In d.c. voltammetry, the detection limit is represented by electrolytic currents of the order of tenths of nanoamperes; at lower values, the signal-to-noise ratio is already too low for obtaining unambiguous results.

One way of improving the signal-to-noise ratio is utilization of a more sensitive measuring method (*e.g.*, a.c. voltammetry or square-wave polarography, see for example ref. 2). These methods are subject to two serious drawbacks, namely, the necessity of employing much more involved apparatus and the fact that with slow charge-transfer reactions the gain in sensitivity is very small and frequently non-existent.[3,4] Another way is to carry out the stripping process under conditions of convective diffusion (stirring, rotating or vibrating electrodes *etc*, see for example ref. 5). The disadvantage of this approach is poorer accuracy and precision, especially if solid electrodes are used. Nonetheless, the application of rotating disk electrodes, either solid or mercury thin-layer electrodes, seems to be very promising.[6] The sensitivity may also be improved by using mercury thin-layer electrodes, because of a more favourable ratio of the active surface to the volume of mercury (see for example ref. 7). There is an additional advantage in increased selectivity, owing to the very narrow peaks obtained.

If the conventional type of apparatus is employed for anodic-stripping voltammetry, there is still the possibility of varying the sensitivity of measurement by means of variations in the solution volume, mercury-drop electrode size, and the pre-electrolysis time, the pre-electrolysis potential being usually determined by the selectivity requirements. The dependence of the anodic peak current, I_a, on the experimental conditions is a complex function and according to Stromberg and Zakharov[8] it may be written in the following form:

$$I_a = a(1 - e^{-b})$$

where

$$a = 3K_1 c_M{}^{\circ} V \frac{1}{r} \quad ; \quad b = 4\pi K_e r^2 \frac{t}{V}$$

K_1 being a proportionality constant, K_e an electrolytic constant depending upon the pre-electrolysis potential and hydrodynamic conditions, $c_M{}^{\circ}$ the initial metal concentration in the solution, V the solution volume, r the mercury-drop radius, and t the pre-electrolysis time.

From analysis of these equations it follows[8] that, for small values of $b (< 0{\cdot}1)$, when V is sufficiently large and t and r are sufficiently small, the peak height is independent of V and is directly proportional to r and t. The concentration in the solution is practically unchanged after pre-electrolysis. For $0{\cdot}1 < b < 3$ the peak height increases with increasing t and V up to a certain limiting value, while the dependence of I_a on r exhibits a maximum at $b = 1{\cdot}26$. For $b > 3$, when V is sufficiently small and t and r sufficiently large, the peak height is independent of t (the metal is practically completely removed from the solution during pre-electrolysis), directly proportional to V and indirectly to r.

In the present paper we have attempted to show that the conditions in the last case ($b > 3$) are advantageous not only for increasing the sensitivity of the method but generally for any stripping determination.

For work with very small volumes, a special microelectrolytic cell had to be constructed, since no convenient microcell has been described in the literature so far. Several microcells have been constructed for polarography,[9–12] amperometric titrations,[10,13–15] coulometry,[16] and chronopotentiometry.[17] The two microcells which have been constructed for stripping analysis, one for volumes of 0·3–0·5 ml[18] and the other for 1–2 ml,[19] still employ volumes that are too large for our purposes, and are actually only miniatures of normal polarographic cells.

EXPERIMENTAL

Reagents

The mercury used was of *pro analysi* purity, further purified by distillation. Water was redistilled in a quartz apparatus.

The mineral acids (H_2SO_4, $HClO_4$) were of *pro analysi* purity.

Stock solutions of $Cu(NO_3)_2$ and $Pb(NO_3)_2$ ($10^{-2}M$) were prepared by dissolving the metals ("extrapur", Soyuzkhimeksport, Moscow) in dilute nitric acid, evaporating to dryness, and dissolving the residue in water. From these stock solutions freshly diluted solutions were prepared daily.

Apparatus

The PO-4 polarograph (Radiometer, Copenhagen) was used for voltammetric measurements. The nitrogen used for deaerating and stirring the electrolysed solutions was freed from oxygen by passage through a column containing zinc amalgam and a 0·2% w/v solution of sodium anthraquinone-2-sulphonate in 1*M* sodium hydroxide, and its flow-rate was measured with a bubble flow-meter. Mercury drops were produced from a 1-ml syringe burette (Manostat, USA), readable to 0·1 μl. In some cases the size of the drops was checked by weighing. The depolarizer solutions were measured with the Agla 0·5-ml syringe burette, readable to 0·2 μl.

The determination of copper in potassium nitrate by atomic-absorption spectrophotometry (AAS) was performed with a Unicam SP 90 spectrophotometer with an air–acetylene flame.

Design of the microelectrolytic cell

The types of microcells proposed by Majer for polarography,[8] which basically consist of a large mercury surface, onto which a drop of solution is placed, are unsuitable because of the instability of the drop and the impossibility of maintaining an inert atmosphere. The best results were obtained with the cell shown in Fig. 1.

The cell consists of a glass U-tube with one arm widened to form an electrolytic space. In the bottom of this space is sealed a platinum contact. The other arm is filled with mercury to provide electrical contact with the platinum wire. The electrolytic space is closed with a stopper with three openings, for the capillary of the salt bridge of the reference electrode, the capillary of the nitrogen inlet, and for nitrogen outlet. The cell itself is placed in a larger glass container and fixed in place with plastic foam. Under normal conditions, the air mantle thus formed around the vessel itself keeps the temperature sufficiently constant. However, if desired, it is very easy to provide the vessel with a constant-temperature mantle.

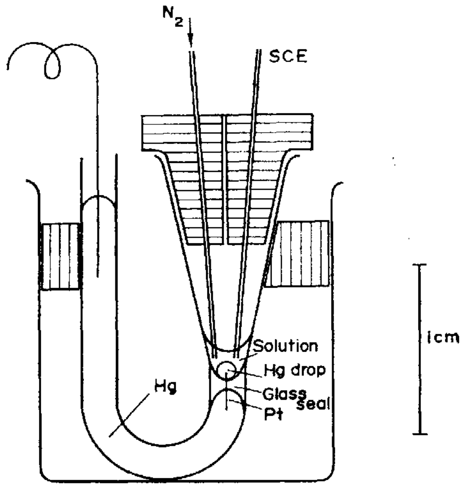


FIG. 1.—The microelectrolytic cell.

The vessel makes possible the stripping analysis of as little as 10 μl of solution, using mercury drops of various sizes as electrodes. Nitrogen serves both for deaerating the solution and for stirring during pre-electrolysis.

Procedure

A mercury drop of the desired size is measured and put on the platinum contact in the bottom of the electrolytic space. Instead of measuring the drops with a syringe burette as in the present paper, it is advantageous to use an ordinary polarographic capillary, which produces drops of fairly reproducible size. Then the solution is measured into the cell, passage of nitrogen is begun, and the solution is electrolysed at a preset potential for a predetermined time. The passage of nitrogen is stopped, electrolysis is continued for a certain time in the quiet solution, and then the dissolution peaks are recorded. Owing to the very small volume of the solution, the deaeration is accomplished in a very short time interval and thus can be performed simultaneously with the pre-electrolysis. Nitrogen is passed above the level of the solution during the electrolysis in the quiet solution and during the potential scan.

In the present paper, the following conditions were utilized, unless stated otherwise: a mercury-drop size of 5 μl, a pre-electrolysis time of 5 min, 30 sec of electrolysis in a quiet solution, a saturated calomel reference electrode (SCE) connected with the cell by a capillary bridge filled with a saturated solution of potassium nitrate and closed with an agar plug (the bridge was connected to the electrode by a ground-glass joint), a nitrogen flow-rate of 20 ml/min, a potential-scan rate of 800 mV/min, a chart speed of 80 mm/min.

All potentials are referred to the SCE. The measurements were performed at 22 ± 0·5°.

Notes for work with the microcell

The capillary for introducing nitrogen should be very fine to prevent splashing of the solution. Care should be taken to prevent contact of the solution with the platinum wire and formation of gas bubbles between the platinum wire and the mercury drop (which can happen during passage of nitrogen at too high a flow-rate). To prevent formation of air bubbles in the orifice of the capillary bridge of the SCE it is advantageous to cover it with a piece of sealed polyethylene tubing when not working. It is advantageous to work with several cells so that new samples can be prepared during the analysis of those already prepared.

RESULTS

The reproducibility of the mercury-drop size was checked by weighing. It was found, from ten measurements with 8-μl drops (0·10872 g), that the maximum relative deviation was 1·33%, mean relative deviation 0·67%, and the standard deviation $8{\cdot}9 \times 10^{-4}$g.

Dilute mineral acids (perchloric, sulphuric) were found to be the best base electrolytes, since they contain relatively the smallest amounts of metallic impurities. The most suitable concentration of the base electrolyte was found to be about 0·1*M*.

Dependence of the peak current on the pre-electrolysis time, potential, and the drop size

It was found that amounts of depolarizer of the order of tens of nanograms in tens of microlitres of solution are completely transferred into the mercury drop (5 μl) in about 4 min of pre-electrolysis at the potential of the depolarizer limiting current. A typical dependence of the peak current on the pre-electrolysis time is shown in Fig. 2.

On the basis of this result, a 5-min pre-electrolysis with a 30-sec electrolysis in the quiet solution was used in all succeeding experiments. It is obvious that in practical applications this value must always be determined for the particular measuring conditions utilized. Experiment showed that the precision improved with increasing pre-electrolysis time, the optimum time being about 4–5 min.

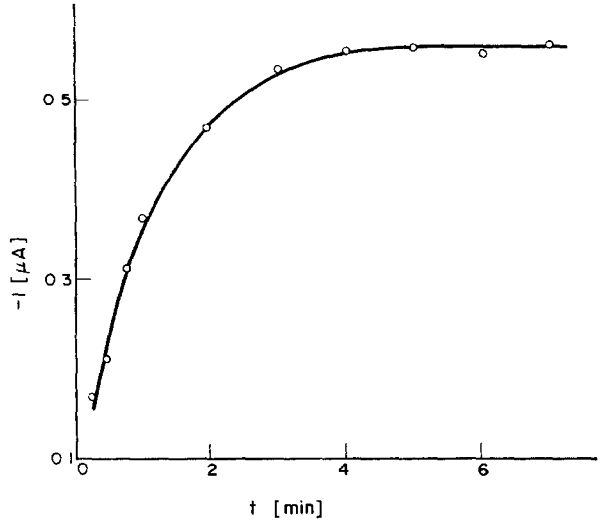


FIG. 2.—The dependence of the lead peak-current on the time of pre-electrolysis. 40 ng of Pb^{2+} in 40 μl of 0·1*M* $HClO_4$, pre-electrolysis potential, −1·5 V. (The pre-electrolysis time given in the graph corresponds to the pre-electrolysis in the nitrogen-stirred solution; this was followed by a 30-sec electrolysis in quiet solution).

The dependences of the copper and lead peak-currents on the pre-electrolysis potential are shown in Fig. 3. This dependence has the shape usually found in stripping analysis, the only difference from that for analysis in larger amounts of solutions being that there is no peak-current increase due to the stirring of the solution by hydrogen evolving at very negative potentials (*cf.* curve *c* in Fig. 3, which has been taken from Fig. 1 of our previous paper[1]). Evolution of hydrogen at higher potentials does not increase the peak current since the depolarizer is already completely electrolysed into the mercury drop under given conditions so that nothing can be gained by increasing the rate of stirring of the solution. In practice the pre-electrolysis potential may, therefore, be set at any value corresponding to complete removal of the depolarizer from the solution under the given working conditions.

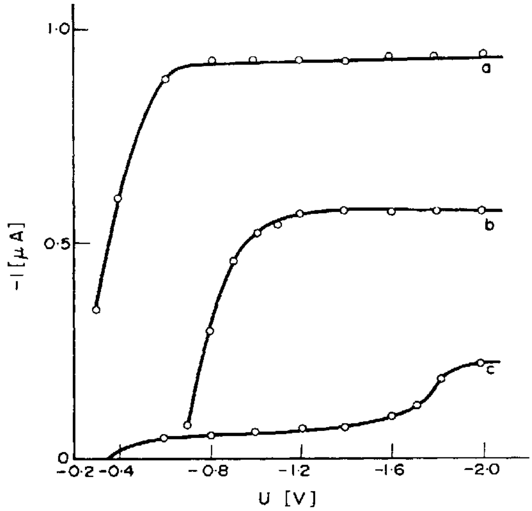


FIG. 3.—The dependence of the copper and lead peak-currents on the pre-electrolysis potential.
(*a*) 40 ng of Cu^{2+} in 0·1*M* H_2SO_4; (*b*) 40 ng of Pb^{2+} in 0·1*M* $HClO_4$; solution volume, 40 μl; 5 min pre-electrolysis. (*c*) 10^{-6}*M* Pb^{2+} in an acetate buffer, 15 ml of solution, 2 min pre-electrolysis, Kemula electrode.[1]

The dependence of the lead peak-current on the mercury-drop size is given in Fig. 4, and is in agreement with the conclusions reached by Stromberg and Zakharov.[8] Unfortunately, the active area or the radius of the mercury drop could not be found since the shape of the drop is determined by the geometry of the bottom of the microcell and only a part of the mercury surface is actually in contact with the solution. In any case, it is evident from the dependence that the sensitivity of determinations increases with decreasing size of the mercury-drop electrode, but that the variations in the drop size will have a progressively greater effect on the reproducibility of determinations as the drop is made smaller.

For large volumes of solution (of the order of tens of millilitres) the dependence of the peak currents on the mercury-drop size is reversed: the current increases with the drop size.[20–23] On further increase of the drop size, a dependence exhibiting a maximum would probably eventually be obtained. Some workers[20,23] actually

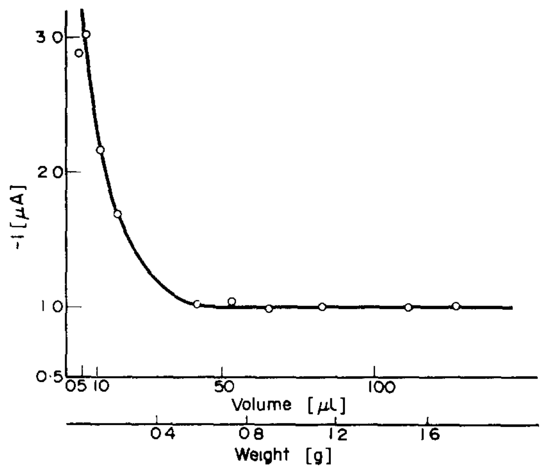


FIG. 4.—The dependence of the lead peak-current on the size of the mercury-drop electrode.

150 ng of Pb^{2+} in 0·03 ml of 0·1*M* $HClO_4$. 10 min pre-electrolysis at a potential of −1·5 V.

found that the peak-current–drop-size dependence reaches a certain limiting value.

In contrast to the conclusions reached by Stromberg and Zakharov,[8] direct proportionality between the solution volume and the peak current has not been found over the volume range 0·01–0·1 ml. There is no change in the sensitivity due to variations of the solution volume within this interval. Apparently, the drop size and consequently the concentration of the depolarizer in the amalgam is the decisive factor, and in comparison the effect of the solution volume is negligible in this interval of very small volumes where all the depolarizer is transferred into the drop during pre-electrolysis.

Reproducibility of results and calibration curves

The reproducibility with the microcell was studied by using small amounts of lead in 0·1*M* perchloric acid. The results are summarized in Table I. It follows that

TABLE I.—THE REPRODUCIBILITY OF DETERMINATIONS OF LEAD IN 0·1*M* $HClO_4$. [2 ng OF Pb^{2+} IN 20 μl OF SOLUTION; MERCURY DROP 5 μl; 5 min PRE-ELECTROLYSIS AT −1·5 V; 1 mm CORRESPONDS TO 4 nA (1 μA FULL SCALE DEFLECTION)].

Peak height *h, mm*	$\bar{h}$, *mm*	Absolute deviation Δ*h, mm*	$\Delta\bar{h}$, *mm*	Relative deviation ε, %	$\bar{\varepsilon}$, %	Standard deviation, *s, mm*
8·0	8·0	0·0	0·5	0·0	6·25	0·74
8·5		0·5		6·25		
6·5		1·5		18 75		
8·0		0·0		0·0		
7·0		1·0		12·5		
9·0		1·0		12·5		
8·0		0·0		0·0		
8·0		0·0		0·0		
8·5		0·5		6·25		
8·5		0·5		6·25		

the reproducibility is good. The lead concentration determined is $4{\cdot}83 \times 10^{-7}M$. If the same amount of lead were to be determined in 10 ml of solution it would correspond to $9{\cdot}6 \times 10^{-10}M$ which is already below the detection limit of the classical stripping determination of lead. There is still the possibility of decreasing by almost one order the amount determined by using the microcell, if a higher polarographic sensitivity is employed.

Calibration curves were determined for copper in $0{\cdot}1M$ sulphuric acid and for lead in $0{\cdot}1M$ perchloric acid in 20 μl of solution, from 1 to 40 ng and 1 to 150 ng, respectively, corresponding to the concentration ranges $7{\cdot}9 \times 10^{-7} - 3{\cdot}1 \times 10^{-5}M$ and $2{\cdot}4 \times 10^{-7} - 3{\cdot}6 \times 10^{-5}M$, respectively. The calibration curves were perfectly linear and passed through the origin. The peaks corresponding to these concentrations are very well developed.

Determination of copper in pro-analysi *potassium nitrate*

As an example of a practical application, copper was determined in pure potassium nitrate. The following conditions were used: a 12% KNO_3 solution in $0{\cdot}1M$ H_2SO_4 was analysed; the analysis was performed in 20 μl of solution, with a drop size of 5 μl, pre-electrolysis time of 5 min and potential of $-1{\cdot}0$ V. The method of standard addition was employed, using 0·02 ml of a standard solution containing 0·5 μg of Cu^{2+}/ml. From four measurements the value found was $3{\cdot}30 \pm 0{\cdot}12 \times 10^{-4}\%$ copper (95% confidence limits).

A parallel determination in a 6% KNO_3 solution by AAS, using an air–acetylene flame and standard solutions containing 0·5–0·2 μg of Cu^{2+}/ml, gave a value of $4{\cdot}8 \times 10^{-4}\%$.

The determination by AAS is just at the detection limit under the given conditions: peaks about 5 mm high were obtained at the maximum sensitivity of the instrument. Moreover, the concentration of potassium nitrate cannot be increased above 6% (the producer of the instrument does not recommend analyses of more concentrated solutions than about 6%, because of difficulties involved in atomizing the entire sample and clogging of capillaries). On the other hand, the stripping determination provided peaks 40–80 mm high at a sensitivity of 1 μA full-scale deflection. The sensitivity of determination can be further increased by using sample solutions more concentrated than 12% and by increasing the sensitivity of the current measurement.

DISCUSSION

As follows from the results above, stripping analysis in very small volumes of solution makes possible determinations of substantially smaller amounts of metals than conventional stripping voltammetry. Of course, the *concentration* determinable is approximately the same. The dependences of the peak current on the working conditions correspond basically to the conclusions arrived at by Stromberg and Zakharov.[8]

Besides the obvious advantages of the stripping microanalysis, which are the possibility of carrying out an analysis even if a very small amount of sample is available, and very low consumption of chemicals, there are several general advantages over conventional stripping voltammetry. The apparatus is very simple and there is no need for any special parts (stationary-drop electrodes, stirrers) in addition to the usual type of polarograph. The deaeration of the solution is very fast and effective.

The mercury drops for the electrodes can be produced by an ordinary polarographic capillary. For this reason, the troubles which frequently occur with the Kemula type of stationary-drop electrode, *e.g.*, air bubbles in the reservoir and the capillary, drop instability, solution penetration into the capillary *etc*, are avoided.

The chief advantage of the microanalysis is that all the depolarizer is transferred into the mercury drop during the pre-electrolysis. In this way all sources of error stemming from variations in the pre-electrolysis time, potential, stirring rate, and temperature are eliminated. The only thing necessary is to find a time sufficient for complete electrolysis and to use a safety margin to provide for variations in the working conditions. These times are relatively short in analyses of very small amounts. Possible defects in the microcell (gas bubbles between the platinum contact and the mercury drop) are easily detectable and removable. The time required for an analysis is shorter with the microcell.

During tests with the microcell it was also found that it is very convenient for cyclic voltammetry; very narrow, sharp, and reproducible peaks were obtained.

Work with the microcell, however, places greater demands on clean and careful work. For measurements at very low concentrations it is desirable to use shielded leads from the electrodes. A disadvantage also lies in the fact that greater accuracy and precision of measuring solution volumes is necessary (as with all micro-techniques). If all these conditions are fulfilled, the accuracy and precision are very good and under optimum conditions even sub-nanogram amounts of certain elements can be determined.

If the method is compared with AAS it is found that stripping microanalysis is more sensitive and precise for certain metals, *e.g.* Cu, Pb, Cd, and that the apparatus is substantially simpler and cheaper. On the other hand, routine determinations by AAS are faster and the method has a broader application. In many cases work with AAS entails fewer difficulties with interferences but, on the other hand, stripping analysis more frequently makes possible simultaneous determinations of several elements and such determinations can be performed more easily. In many cases, stripping analysis makes possible determinations in very concentrated matrix solutions while in AAS very concentrated salt solutions cannot be used. As can be seen from the discussion, stripping analysis and AAS can often complement each other in the broad spectrum of routine determinations.

Zusammenfassung—Es wird eine kurze Besprechung von Problemen gebracht, die mit Steigerung der Empfindlichkeit anodischer Abscheidungsbestimmungen verbunden sind. Es wurde eine neue Mikrozelle für anodische Abscheidungsvoltampèremessung in Lösungsvolumen bis hinunter auf etwa 0,01 ml konstruiert. Es wurde die Wirkung des Lösungsvolumens, der Quecksilbertropfengrösse der Elektrode und der Zeit und des Potentials vor Elektrolyse auf die Empfindlichkeit der Bestimmungen untersucht, und es wird die Reproduzierbarkeit der Ergebnisse für Bestimmungen von Blei in Mineralsäuren wiedergegeben. Es wurde gefunden, dass Nanogrammengen schwerer Metalle leicht auf diese Weise bestimmt werden können. In Bestimmungen von 2 ng Pb^{2+} in 0,02 ml Lösung waren die Ergebnisse 2,00 ± 0,13 ng (95% Vertrauensgrenzen), die mittlere relative Abweichung war 6,3%. Mikroanalyse für Abscheidung zur Bestimmung von Kupfer in KNO_3 wurde mit atomischer Absorptionsspektralphotometrie verglichen. Es werden Vorteile und Nachteile der Abscheidungsvoltampèremessung auf die Grösst- und Kleinstabscheidungen besprochen.

Résumé—On présente une brève discussion des problèmes liés à l'accroissement de la sensibilité des dosages par dissolution anodique. On a construit une nouvelle microcuve pour la voltammétrie de dissolution anodique dans des volumes de solutions descendant jusqu'à 0,01 ml environ. On a étudié l'influence du volume de solution, de la dimension de l'électrode à goutte de mercure, et du temps et du potentiel de pré-électrolyse sur la sensibilité des dosages et l'on donne la reproductibilité des résultats pour les dosages du plomb dans les acides minéraux. On a trouvé que des quantités de l'ordre du nanogramme de métaux lourds peuvent être aisément déterminées de cette manière. Dans le dosage de 2 ng de Pb^{2+} dans 0,02 ml de solution, les résultats ont été de 2,00 ± 0,13 ng (limite de confiance 95%), la déviation relative moyenne étant 6,3%. Pour le dosage du cuivre dans KNO_3, la microanalyse par dissolution a été comparée à la spectrophotométrie d'absorption atomique. On discute des avantages et des désavantages de la voltammétrie de dissolution aux échelles macro et micro.

REFERENCES

1. L. Zieglerová, K. Štulík and J. Doležal, *Talanta*, 1971, **18**, 603.
2. A. M. Bond, *Anal. Chem.*, 1970, **42**, 1165.
3. D. E. Smith, in *Electroanalytical Chemistry*, ed. A. J. Bard, Vol. 1, p. 31. Dekker, New York, 1966.
4. B. Breyer and H. H. Bauer, *Alternating Current Polarography and Tensammetry*, Interscience, New York, 1963.
5. E. Barendrecht, *Nature*, 1958, **191**, 241.
6. M. Kopanica and F. Vydra, *J. Electroanal. Chem.*, 1971, **31**, 175.
7. V. A. Igolinskii and A. G. Stromberg, *Zavodsk. Lab.*, 1964, **30**, 656.
8. A. G. Stromberg and M. S. Zakharov, *Metody Analiza Khimicheskikh Reaktivov i Preparatov*, p. 16. IREA, Moscow, 1963.
9. V. Majer, *Polarografické rozbory*, p. 91. Tech. Věd. Vydav, Prague, 1952.
10. A. Langer, *Ind. Eng. Chem., Anal. Ed.*, 1945, **17**, 454.
11. N. M. Vlasco and B. M. Kopytin, *Biokhimyia*, 1950, **15**, 94.
12. Yu. S. Lyalikov and R. S. Tyurin, *Zh. Analit. Khim.*, 1969, **24**, 186.
13. J. T. Stock, *Amperometric Titrations*, p. 108. Interscience, New York, 1965.
14. S. Rosenberg, J. C. Perrone and P. L. Kirk, *Anal. Chem.*, 1950, **22**, 1186.
15. M. N. Petrikova and I. P. Alimarin, *Zh. Analit. Khim.*, 1957, **12**, 462.
16 S. S. Lord, R. C. O'Neil and L. B. Rogers, *Anal. Chem.*, 1952, **24**, 209.
17. R. T. Iwamoto, R. N. Adams and H. Lott, *Anal. Chim. Acta*, 1959, **20**, 84.
18. L. Underkofler and I. Shain, *Anal. Chem.* 1961, **33**, 1966.
19. L. Jenšovský, *Chem. Tech.*, 1961, **13**, 519.
20. W. Kemula, Z. Kublik and S. Glodowski, *J. Electroanal. Chem.*, 1959, **1**, 91.
21. J. G. Nikelly and W. D. Cooke, *Anal. Chem.*, 1957, **29**, 933.
22. E. N. Vinogradova and G. V. Prokhorova; *Zavodsk. Lab.*, 1960, **26**, 41.
23. S. I. Sinyakova and Shen-Yu-Chi, *Dokl. Akad. Nauk USSR*, 1960, **131**, 101.

Talanta, 1972, Vol. 19, pp. 1295 to 1300. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF AND DIFFERENTIATION BETWEEN CASSITERITE AND SILICATE-BOUND TIN IN SILICATE ROCKS CONTAINING TRACES OF TIN

J. AGTERDENBOS and J. VLOGTMAN
Laboratory for Analytical Chemistry, State University, Croesestraat 77A, Utrecht, Holland

(*Received* 5 *December* 1971. *Accepted* 10 *March* 1972)

Summary—A simple, sensitive and reproducible method is described for the determination of tin in silicate rocks at the ppm level. By applying a selective decomposition it seems possible to differentiate between tin present in the silicate lattice, in readily-accessible cassiterite (SnO_2) and in cassiterite enclosed in the silicate. The final determination is made by extraction and photometry with phenylfluorone. Results for total tin agree well with those obtained by X-ray fluorescence.

TIN OCCURS in many silicate rocks, often in concentrations far below 100 ppm. Part of this tin may be a constituent of the silicate lattice ("lattice-bound tin") and another part may be present in the form of cassiterite, tin(IV) oxide, and knowledge of their proportions is useful to geochemists, both for prospecting and for scientific studies.

Some of the methods for the determination of tin in ores have been described and compared by Jeffery.[1] With methods such as emission spectrography and X-ray fluorescence the total amount of tin is determined without risk of loss due to incomplete destruction, but the results do not differentiate between different types of tin. These techniques are not sensitive enough at the lower levels of tin concentration to be studied here.

Other techniques require a decomposition step. For the final determination several spectrophotometric procedures have been described. After preliminary experiments with Wood's[2] galleïne procedure, which did not give satisfactory results in our hands, we successfully used the method described by Gilbert and Sandell.[3] It consists of a separation of tin from other elements (especially germanium) by extraction of tin(IV) iodide into benzene, stripping into water and final determination with phenylfluorone. Atomic absorption may also be used,[4,5] but was not investigated in our study.

The ignition of sample with ammonium iodide at 400–500° (Caley and Burford[6]) quantitatively converts cassiterite into tin(IV) iodide, but lattice-bound tin is not attacked. The silicate lattice may be decomposed by treatment with a mixture of hydrofluoric and sulphuric acids, or perchloric and nitric acids. Cassiterite does not react with these mixtures. In this way "fresh" tin(IV) oxide is formed, and this may then be similarly treated with ammonium iodide to give tin(IV) iodide. "Fresh" tin(IV) oxide is also converted into tin(IV) iodide by hydriodic acid solution; cassiterite is not attacked by this reagent. These differentiations form the basis of the proposed method, which allows tin down to 3 ppm to be determined.

Other decomposition procedures include fusion with sodium peroxide, with potassium pyrosulphate and with a sodium carbonate–sulphur mixture.[1] None of these procedures enables tin present as cassiterite and tin present in the silicate lattice to be differentiated, and they do not seem useful at tin levels below 20 ppm. Total tin may be found by attacking the sample with hydrofluoric–nitric acid mixture, and then heating it with ammonium iodide.

EXPERIMENTAL

Apparatus

Destruction unit. Pyrex-tube 2 cm wide and 25 cm long fitted with a 40-cm Liebig condenser.

Platinum crucibles. About 20 ml capacity.

Reagents. All reagents were of analytical-reagent grade.

Destruction mixture. Mix two volumes of 40% hydrofluoric acid with one volume of 65% nitric acid.

Sulphuric acid, concentrated and 0·25M.

Ammonium iodide.

Twice-distilled demineralized water.

Hydriodic acid, 57% and 2·5M.

Wash liquid. Ammonium iodide (15 g) dissolved in 20 ml of 2·5*M* hydriodic acid.

Benzene.

Potassium hydrogen phthalate–hydrochloric acid buffer, pH 2·6.

Gum arabic solution, 1%. Discard the solution when it becomes turbid.

Phenylfluorone solution, 0·01%. Dissolve 10 mg of reagent in 1 ml of 1·2*M* hydrochloric acid and 100 ml of ethanol. The solution is stable for two months.

Sodium sulphite solution, 0·3M.

Standard solution of tin(IV) 0·1%, in 3M sulphuric acid. Dissolve 0·50 g of tin in 20 ml of concentrated sulphuric acid, cool, add 5 ml of 30% hydrogen peroxide, heat to fumes of sulphur trioxide, cool, and dilute to 500 ml, with addition of 65 ml of 18*M* sulphuric acid.

Procedures

Destruction with hydrofluoric–nitric acid mixture. Weigh 1 g of sample in a weighed platinum crucible and place in a heating-block. Add 1 ml of the destruction mixture, and wait until the violent reaction is finished. Heat gently on an electric hot-plate, and add 1 ml of the destruction mixture. Repeat this until the silicate is dissolved (generally two or three additions are necessary). Heat to dryness and fume the residue three times with 2-ml portions of sulphuric acid. Cool and weigh the platinum crucible. Transfer the residue into a mortar and grind to a fine powder.

Decomposition with ammonium iodide. Transfer to the destruction unit an exactly weighed amount (as much as possible) of the powder resulting from the procedure above and mix it thoroughly with 10 g of ammonium iodide. Place the lower part of the tube (about 6 cm) in an electric oven heated at about 480°. Heat for 1 hr, and cool.

Extraction. Transfer 20 ml of 2·5*M* hydriodic acid and 5 g of ammonium iodide into the destruction unit. After dissolution is complete add 7 ml of benzene and extract for 3 min. After both layers have separated, transfer 5 ml of the benzene layer into a 100-ml separating-funnel, add 5 ml of wash liquid and shake for 30 sec. After separation, discard the water layer and add 5 ml of 0·25*M* sulphuric acid to the funnel. Shake for 2 min to transfer the tin into the water layer.

Spectrophotometric determination. Transfer the water layer into a 25-ml volumetric flask, using 3 ml of water to rinse the separating-funnel. Heat in a water-bath to evaporate any benzene not completely removed by the separation. Cool, add some drops of sodium sulphite solution to reduce iodine (formed during the destruction). Add successively 10 ml of buffer, 1 ml of gum arabic solution, and 5 ml of reagent solution. Dilute to the mark, mix, and after 15 min measure in a 1-cm cuvette at 510 nm against water as reference. Subtract the absorbance of a blank run on the same day. Prepare a calibration curve in the usual way.

Destruction of "fresh" tin(IV) oxide with hydriodic acid, extraction and determination. Transfer an exactly weighed amount (as much as possible) of the powder from the HF/HNO_3 treatment into a reagent tube with ground-glass stopper. Add 6 ml of concentrated hydriodic acid and heat in a water-bath for 5 min at 100°. Cool, add 7 ml of benzene, and continue with the extraction and spectophotometric determination.

Note. The procedures given are applicable to samples containing about 3–15 ppm of tin. If more tin is present, smaller samples may be used or a smaller part of the benzene layer may be transferred into the separating-funnel, or a combination of both modifications may be used. The amount of ammonium iodide should be at least ten times the amount of sample and at least 2 g. If less than 10 g of ammonium iodide are used in the destruction, a correspondingly larger amount of ammonium iodide should be used in the extraction in order to reach the required concentration of this reagent.

RESULTS

Tin has been determined in some types of geological sample, such as granite, biotite and muscovite by the proposed method. The results are given in Table I, and compared with those obtained with X-ray fluorescence by van der Weyden.[7] The precision of the latter results is reported to decrease from about 5 or 10 ppm at the lower tin levels, to about 5 or 10% at the higher tin-levels.

TABLE I.—RESULTS OF EXPERIMENTS

	Amount of tin, *ppm*				
	X-ray fluorescence	Chemical methods			
Sample	1 Total tin	2 Total tin	3 Lattice-bound tin	4 Tin present in cassiterite, calculated (2 − 3)	5 Tin in free accessible cassiterite
1 granite	80	74; 77; 75	57; 61; 62	15	3·2; 2·7; 2·9
2 granite	15	20; 22; 18; 20; 18	7·3; 8·4; 7·9; 9·0; 7·5	12	—
3 granite	5	2·4; 4·8; 3·3	2·6	0·9	—
4 granite	18	27; 27	5·1; 5·3	22	2·9
5 biotite	15; 20	27	4·7	22	2·7
6 muscovite	70	83	52	31	36
7 granite	5	2·9	2·6	0·3	1·0
8 biotite	15; 15	20	9·0	11	1·8
9 granite	10	12	3·5	8·5	1·4
10 biotite	40; 40	36	11	25	5·3
11 granite	5	11	2·8	8·2	1·2
12 biotite	55; 65	58	28	30	2·6
13 granite	5	4·6	3·5	1·1	2·2
14 biotite	55; 65	62	55	7	14
15 granite	5	8·2	2·8	5·4	2·2
16 biotite	30; 35	27	9·0	18	2·2
17 muscovite	40; 50	35	12	23	2·8
18 granite	13	34; 30; 30	12	19	11
19 biotite	440; 425	463; 457	222; 229	234	73
20 granite	40	40	14	26	21
21 biotite	490; 470	440	345	95	109
22 titanite	—	32; 38; 37	8·0	28	11

The results obtained by treatment with hydrofluoric–nitric acid and subsequent ignition with ammonium iodide are given in column 2. Results obtained after treatment with hydrofluoric–nitric acid with subsequent reaction with hydriodic acid are given in column 3 and the results obtained by treating the sample with ammonium iodide only are given in column 5.

DISCUSSION

Extraction and spectrophotometric determination

The extraction is promoted by a high concentration of hydrogen ions and iodide ions and by a high electrolyte concentration. The different decomposition procedures led to different concentrations of those species, but with each of the resulting solutions practically the same calibration curves were obtained. The absorbance of the blank increased with time (by *ca.* 0·10–0·15 in two months) and varied from day to day by up to 0·01.

Iodine formed from the hydriodic acid and ammonium iodide used for decomposition did not interfere, nor did fluoride up to 0·01*M*, though higher concentrations did. It is important to ensure removal of the bulk of the fluoride if hydrofluoric acid is used.

Decomposition with ammonium iodide

Caley and Burford[6] observed that heating of cassiterite with a 10- or 15-fold excess of ammonium iodide resulted in complete removal of both compounds. They suggested that a determination of tin based on this reaction was possible.

Wood[2] and some others used the method for the determination of cassiterite in soils and sediments. Wood used a twofold excess of ammonium iodide, but neither he nor later investigators reported recovery figures. Little attention has been given to the possibility that the tin(IV) iodide may be lost because of its volatility. An exception is Kerr (quoted by Jeffery[1]), who designed a special apparatus to prevent evaporation losses. We performed 25 recovery experiments under various conditions with about 20 μg of cassiterite or an equivalent amount of tin(IV) solution, added to granite. The results gave bad recoveries (50–80% in most cases) if heating was performed in reagent tubes cooled with moistened cotton-wool and in most cases with an ammonium iodide–sample ratio 2:1.

Results, given in Table II, were obtained with the procedure described above. In these experiments the cassiterite used was supposed to have a tin(IV) oxide content between 90 and 95%. It was therefore concluded that the recovery was practically quantitative.

TABLE II.—RECOVERY EXPERIMENTS WITH DIFFERENT AMMONIUM IODIDE–SAMPLE RATIOS.

Amount of granite, *g*	Amount of ammonium iodide, *g*	Ratio, ammonium iodide–sample	Recovery*, %
0·200	2·0	10:1	90
0·130	first 1·3 then 0·7	first 10:1 then 5:1	91
0·130	2·0	15:1	90
0·100	2·0	20:1	89

* The cassiterite was assumed to contain about 90–95% tin(IV) oxide. About 20 μg of cassiterite were added in each experiment.

Reaction of tin(IV) oxide with hydriodic acid

It was also found by Caley and Burford[8] that tin(IV) oxide reacts with concentrated hydriodic acid at 90–100° as follows:

$$SnO_2 + 4HI \rightarrow SnI_4 + 2H_2O$$

Other insoluble oxides do not show any characteristic reactions with this acid. When we treated "fresh" tin(IV) oxide with warm concentrated hydriodic acid, no reaction seemed to occur, but the solid became voluminous. This phenomenon could be explained only by the formation of tin(IV) iodide. Indeed, on shaking the reaction product with benzene the solid disappeared instantaneously and tin was detected in the benzene layer. With cassiterite no reaction took place. This difference in behaviour suggested the possibility of differentiation between cassiterite and lattice-bound tin, because as we saw before, lattice-bound tin may be converted into "fresh" tin(IV) oxide by hydrofluoric–nitric acid mixture.

The time of warming the solution was found to be very important. We performed therefore a number of recovery experiments with different amounts of tin(IV) oxide or tin(IV) solution. They only gave good recoveries when the solution was warmed for not much more than 5 min. Some of the results are given in Table III. The reason for the incomplete recovery was not investigated but it is suggested that a partial reduction to tin(II) takes place.

TABLE III.—INFLUENCE OF THE TIME OF WARMING WITH HYDRIODIC ACID ON THE RECOVERY.

Tin added as	Amount of added tin, *μg*	Amount of hydriodic acid, *ml*	Time of warming, *min*	Recovery, %
Tin(IV) oxide	40·5	2	60	68
Tin(IV) oxide	21·9	2	30	86
Tin(IV) oxide	17·7	2	15	89
Tin(IV) oxide	18·4	3	5	98
Tin(IV) oxide	18·4	5	5	103
Tin(IV) oxide	565·2	5	5	99
Tin(IV) solution	19·3	2	0	99
Tin(IV) solution	9·6	2	2	105
Tin(IV) solution	14·3	2	5	96
Tin(IV) solution	7·2	6	5	104
Tin(IV) solution	14·3	2	15	90
Tin(IV) solution	19·3	2	30	71
Tin(IV) solution*	5·9	6	5	102
Tin(IV) solution*	5·9	6	5	91
Tin(IV) solution*	5·9	6	5	95

* The tin solution was added to about 1 g of a granite with known content of lattice-tin. Destruction with hydrofluoric–nitric acid was followed by the treatment with hydriodic acid.

After the treatment with hydrofluoric–nitric acid some hydrofluoric acid is left in the reaction product and too large amounts of it may interfere. Fuming the residue with sulphuric acid is generally applied to remove hydrofluoric acid but it is a well-known fact that the resistance to dissolution of many products is greatly increased if they are exposed to high temperatures. Therefore it seemed possible that the fuming might influence the reactivity of the "fresh" tin(IV) oxide. Consequently some experiments were performed with known amounts of tin added to granite, with fuming repeated various numbers of times. The results showed that fuming between one and five times did not significantly change the recovery, which was close to 100%.

Interpretation of the results

The replicate experiments for the total tin determination (Table I) show a standard deviation of about 1·3 ppm at the 3·5 ppm level (3 variates) 2 ppm at the 20–40-ppm level ($n = 10$) and 3 ppm at the 75-ppm level ($n = 3$). For the lattice-bound tin standard deviations of about 1 ppm at the 8-ppm level ($n = 5$) and 3 ppm at the 60-ppm level ($n = 3$) were found. The contribution to the total error by the extraction and spectrophotometric procedure depends on the final concentration of the sample solution. It varies from about 20% for 3 ppm to 4% for 15 ppm and more. The absolute values for the total tin should agree with the X-ray fluorescence results. Within the limits of error expected the agreement is satisfactory, except for sample 18. No explanation for the deviation found here can be given, except for an untraced error in one of the measurements.

The figures in columns 4 and 5 would be expected to be equal. In many cases rather large deviations have been found, however. To explain this, it should be realized that part of the cassiterite may be occluded in the silicate lattice and therefore may be inaccessible to the ammonium iodide if the sample is ignited with this reagent. It is suggested therefore that the differences between the figures given in columns 4 and 5 give the amount of cassiterite which is more or less enclosed in the silicate lattice.

We conclude that for the determination of the total tin, the destruction described here gives good results and that it may be used at much lower concentrations than X-ray fluorescence can. Moreover it may also allow differentiation between the various types of tin present in the rock: tin bound in the silicate lattice, tin present as cassiterite and readily accessible to reaction with NH_4I, and tin present as cassiterite enclosed in the silicate lattice.

For the determination of cassiterite in silicate rocks the procedures using only ammonium iodide probably often give low results, because they do not take account of the fact that part of the cassiterite is enclosed within the silicate lattice.

Acknowledgement—We express our thanks to Drs. C. H. van der Weyden of the Vening Meinesz Laboratorium voor geochemie en mineralogie of this University. He suggested that we do some work on the analysis of tin with a purely chemical method, put at our disposition his results of the X-ray fluorescence measurements and had valuable talks with us on the geochemical problems we encountered.

Zusammenfassung—Ein einfaches, empfindliches und reproduzierbares Verfahren zur Bestimmung von Zinn im ppm-Bereich in Silikatgesteinen wird angegeben. Durch Verwendung eines selektiven Aufschlusses scheint es möglich, zwischen im Silikatgitter eingebautem Zinn, zwischen gut angreifbarem Cassiterit (SnO_2) und im Silikat eingeschlossenem Cassiterit zu unterscheiden. Die endgültige Bestimmung wird mittels Extraktion und Photometrie mit Phenylfluoron ausgeführt. Die Ergebnisse für das Gesamtzinn stimmen gut mit denen der Röntgenfluoreszenz überein.

Résumé—On décrit une méthode simple, sensible et reproductible pour le dosage de l'étain dans des roches aux silicates au niveau de la p.p.m. En appliquant une décomposition sélective, il semble possible de différencier l'étain présent dans le réseau de silicate, dans la cassitérite aisément accessible (SnO_2) et dans la cassitérite enrobée dans le silicate. On effectue le dosage final par extraction et photométrie à la phénylfluorone. Les résultats pour l'étain total sont en bon accord avec ceux obtenus par fluorescence de rayons X.

REFERENCES

1. P. G. Jeffery, *Chemical Methods of Rock Analysis*, pp. 435–445. Pergamon, Oxford, 1970.
2. G. A. Wood, *Symposium de exploracion geoquimica, Congresso geologico internacional XX^a Sesión Ciudad de México*, 1956, 461.
3. D. D. Gilbert and E. B. Sandell, *Microchem. J.* 1960, **4**, 491.
4. B. Moldan, I. Rubeška, M. Mikšovský and M. Huka, *Anal. Chim. Acta*, 1970, **52**, 91.
5. G. D. Christian and F. J. Feldman, *Atom Absorption Spectroscopy, Applications in Agriculture, Biology and Medicine*, pp. 403–407. Wiley, New York, 1970.
6. E. R. Caley and M. G. Burford, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 114.
7. C. H. van der Weyden, private communication.
8. E. R. Caley and M. G. Burford, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 63.

Talanta, 1972, Vol. 19, pp. 1301 to 1308. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF MANGANESE BY ATOMIC-FLUORESCENCE SPECTROSCOPY USING A CARBON-FILAMENT ATOM-RESERVOIR

L. EBDON,* G. F. KIRKBRIGHT AND T. S. WEST
Department of Chemistry, Imperial College of Science and Technology,
London, SW7 2AY, U.K.

(*Received* 4 *February* 1972. *Accepted* 3 *March* 1972)

Summary—The atomic-fluorescence characteristics of manganese heated on a carbon-filament atom-reservoir (CFAR) are described and compared with (*a*) the atomic-absorption behaviour of the element on the same filament apparatus, and (*b*) its fluorescence behaviour in a separated air–acetylene flame. By fluorescence at 279·5 nm, using 1-μl samples, manganese may be determined down to 0·6 pg (6×10^{-4} ppm) by use of an electrodeless discharge lamp source (3 pg or 3×10^{-3} ppm by absorption, and 20 ng or 1×10^{-2} ppm by flame emission at 403 nm). The effects of fourteen representative cations and anions examined showed no interference at 10-fold and 100-fold levels and serious interference only from magnesium at the 1000-fold level, with *ca.* 10% suppression from Cr, V, Na and K. No fluorescence signals were observed at any wavelength other than 279·5 nm when the CFAR device was used.

PREVIOUS REPORTS from this laboratory have demonstrated the advantages of atomic-fluorescence spectroscopy (AFS) as a sensitive and selective analytical technique, and some applications and advantages of the carbon-filament atom-reservoir (CFAR) have been reported both in AFS and atomic-absorption spectroscopy (AAS).[1] We have recently reported the analytical behaviour of manganese in AFS using an air-acetylene flame[2] and by AAS using a carbon-filament atom-reservoir.[3] The study of the atomic-fluorescence characteristics of manganese in the flame when a high-intensity source was used indicated that manganese may be determined with sensitivity *ca.* one order of magnitude higher than that attainable by flame emission or AAS, and with good selectivity; only magnesium was found to interfere chemically, and scattering interference was observed in the presence of high concentrations of several refractory elements. Although the limits of detection obtained when using AAS with the carbon-filament atom-reservoir or AFS with the air–acetylene flame corresponded to the same solution concentration of manganese, only 5 μl of sample were required for the CFAR and thus a gain of several orders of magnitude in the absolute limit of detection was attainable. A study of interferences when the carbon-filament device was used, indicated six ions which interfered at the 100-fold excess level and with two exceptions, vanadium and magnesium, the interfering ions differed from those reported for the flame cell. In this communication the determination of manganese by using AFS and a CFAR is reported, and the results are compared with our earlier reports of the determination of manganese to illustrate the advantages of both atomic fluorescence and the carbon filament technique.

---

* Present address: Chemistry Department, Makerere University, P.O. Box 7062, Kampala, Uganda.

EXPERIMENTAL

Apparatus

The carbon-filament atom-reservoir, Unicam SP 900A and Telequipment storage oscilloscope described previously were used.[3] The a.c. amplification system of the SP 900A was replaced by a fast response d.c. detection system employing an independent EHT supply and taking the photomultiplier output direct to the oscilloscope amplifier as recently reported.[4] Both a manganese hollow-cathode lamp (Atomic Spectral Lamps Pty, Ltd.) as used in the AAS work with the CFAR,[3] and an electrodeless discharge lamp, similar to that used in the previous AFS work,[2] were employed as spectral sources. The optical system used for the atomic-absorption studies[3] was used, with the sole modification that the source and lens were moved to be at 90° to the CFAR–monochromator optical axis. This was achieved by placing the source and lens above the filament and focussing the light from the source down on to the filament.[5] This arrangement, although not ideal, as the lens has to be periodically cleaned to remove deposited carbon, was the most suitable for limited-field viewing. Limited-field viewing has been shown, both in this study and previously,[5] to decrease interferences greatly in the carbon-filament technique.

Reagents and procedure

All reagents were of analytical-reagent grade and the water used was glass-distilled and then demineralized. The water used to prepare the solutions, and the reagents used in the interference studies, were periodically checked for contamination by manganese.

The sample pipette and all glassware were treated with "Repelcote" as described previously.[6]

The procedure followed in routine determination was the same as that described previously,[3] but additionally the EHT was set to a previously determined optimum voltage.

RESULTS AND DISCUSSION

Use of a hollow-cathode lamp as excitation source

Usually hollow-cathode lamps operated at typical powers suitable for AAS would not be regarded as sufficiently intense for atomic-fluorescence studies with flame cells. However, because of the low background emission of the carbon-filament atom-reservoir at the time of measurement of the manganese fluorescence signal, appreciable manganese atomic fluorescence was observed when a conventional manganese hollow-cathode lamp was used as source.

The optimum parameters for the determination of manganese by AFS at 279·5 nm were established. The variation of fluorescence signal with filament voltage, for 2 ng of manganese, is shown in Fig. 1. The optimum filament voltage used was *ca.* 11 V. The variation of signal (for 2 ng of manganese) with argon (shielding-gas) flow-rate is shown in Fig. 2. The optimum argon flow-rate was shown to be 3·8 l./min. As expected, the fluorescence signal at 279·5 nm increased as the hollow-cathode lamp current was increased, and the maximum recommended current (30 mA) was used. The fluorescence signal also showed a marked increase as the monochromator slit was opened. The continuum intensity from the glowing filament increased as the slit was opened and therefore the slit-width employed, 0·35 mm, was chosen to give the most favourable ratio of AFS signal to continuum background intensity. This slit-width corresponded to a spectral band-pass of *ca.* 2·4 nm. The optimum value of the EHT was found to be 900 V, and the time-base used on the oscilloscope was 100 msec/cm.

Under these optimum conditions, the detection limits for manganese (signal-to-noise ratio 2:1) at 279·5 nm were 0·001 μg/ml with 5 μl of sample and 0·003 μg/ml for 1-μl samples, *i.e.*, an absolute limit of detection of 3 pg. This limit is of the same order as that previously reported (5 pg) for manganese atomic fluorescence, using a hollow-cathode lamp and the carbon-filament atom-reservoir, but different instrumentation.[7]

Linear calibration graphs were obtained in the region from 5 to 300 pg of manganese.

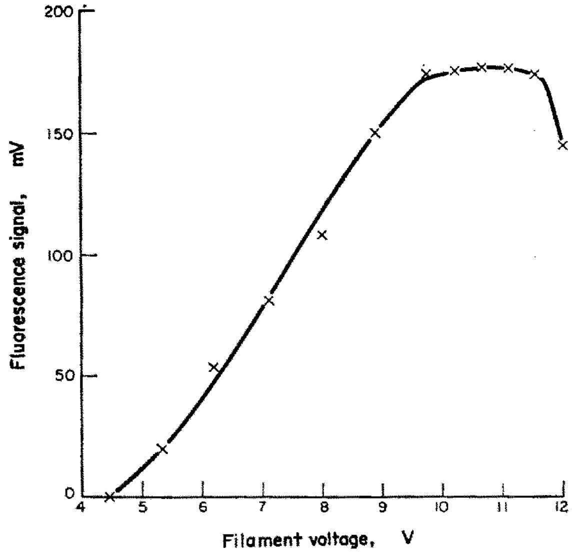


FIG. 1. –Effect of filament voltage on manganese atomic-fluorescence signal at 279·5 nm, using a hollow-cathode lamp source.

The growth curve for manganese atomic fluorescence under these conditions is shown in Fig. 3. The growth curve shows that scatter of the source radiation occurs when more than ca. 0·25 μg of manganese is present. By using the radiation at 283·3 nm from a lead lamp it was shown that with below 0·25 μg of manganese, scatter was not the cause of the signals noted above and no signal was observed from even 5×10^{-8} g of manganese at the 283·3 nm lead line.

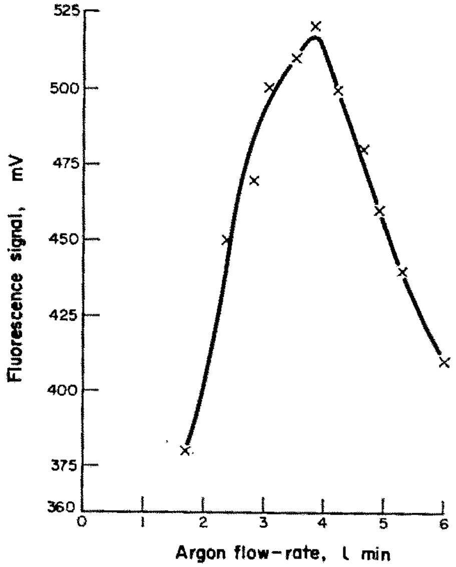


FIG. 2.– Effect of argon flow-rate on manganese fluorescence signal at 279·5 nm, using a hollow-cathode lamp source.

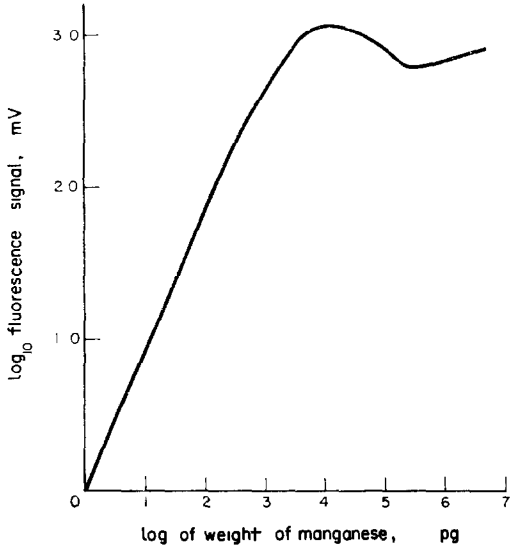


Fig. 3.—Growth curve for manganese atomic-fluorescence at 279·5 nm, using a hollow-cathode lamp source.

Use of an electrodeless discharge lamp (EDL) as source

The preparation, operation and characteristics of manganese electrodeless discharge lamps have previously been described.[2] The optimum argon shielding-gas flow-rate, filament voltage and monochromator slit-width were found to be the same as those reported above for the hollow-cathode lamp source. The optimum EHT for best signal-to-noise ratio was found to be 950 V. The optimum EDL lamp power was 50 W, as previously. The limit of detection (signal-to-noise ratio 2:1) for a 5-μl sample was found to be 0·2 ng/ml, *i.e.*, an absolute limit of detection of 1 pg of manganese. When a 1-μl sample was used an 6 ng/ml solution corresponded to the limit of detection *i.e.*, an absolute limit of detection of 0·6 pg.

The reproducibility of the signals obtained was poorer than that for manganese atomic-absorption with use of the filament. It appears that the short-term noise from the source contributes an additional factor. The reproducibility (95% confidence level) of the signal obtained from any single solution was $\pm 5\%$.

Fluorescence signals at other wavelengths

Attempts to observe manganese atomic fluorescence at wavelengths other than 279·5 nm were unsuccessful with both sources. Particular attention was paid to examination at all the lines at which atomic fluorescence was observed when a flame cell was used).[2] It was not unexpected that fluorescence from the two Mn(II) triplets was not observed. Although the ion line-emission from the electrodeless discharge lamp source was present, as shown by our previous observation of ionic fluorescence of manganese at 257·6 nm in flames,[2] no such emission was observed here because the CFAR does not cause ionization of manganese (the first Mn ionization potential is 7·4 eV). It was not possible to observe atomic fluorescence at 403 nm because of the high continuum intensity from the glowing filament at this longer wavelength; any

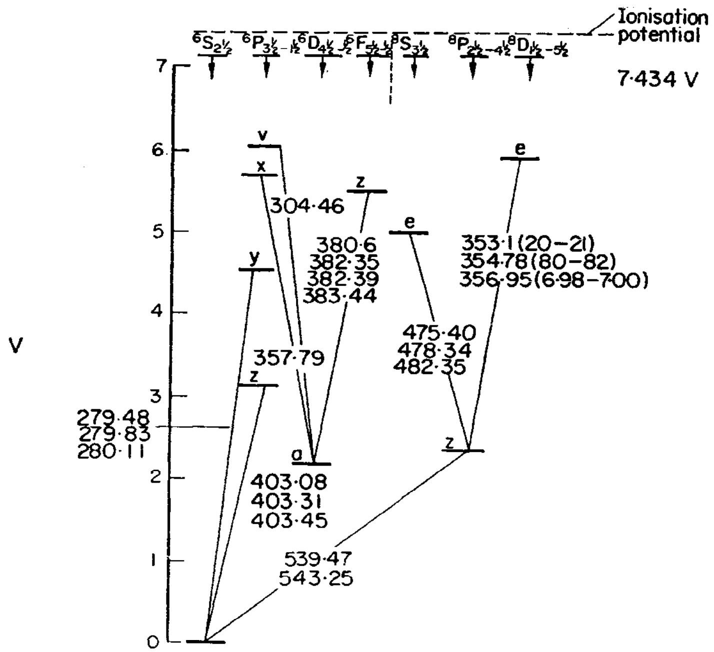


FIG. 4.—Simplified Grotrian diagram for manganese.

fluorescence signal could not, with the d.c. instrumentation employed, be distinguished from the continuum. Study of the simplified Grotrian diagram for manganese (Fig. 4) shows that the fluorescence observed in the flame cell[2] at 304·5, 357·8 and 383·4 nm probably arises from thermally assisted resonance fluorescence. In the air–acetylene flame sufficient energy exists to provide a small population in the lower energy state ($a^6D_{2\frac{1}{2}}$). It is obvious, however, that the carbon filament does not produce sufficient energy (greater than 2 eV is required) to populate this level significantly. This conclusion is in agreement with the estimated temperature above the filament[8] and results obtained for atomic-absorption studies on iron.[4]

Use of nitrogen as shielding gas

The use of nitrogen as shielding gas was investigated and the signals were compared with those obtained with argon. The intensity of atomic-fluorescence signal at 279·5 nm when nitrogen was used was found to be *ca.* 1/16 that obtained with argon as shielding gas. This is to be expected from the much larger quenching cross-section of nitrogen. When a carbon rod is used in the determination of lead in matrices prone to scatter, the fluorescence intensity ratio is 13:1 between argon and nitrogen-shielded rods, and it has been suggested[9] that to a good approximation the scatter signal could be nullified by subtracting the signal obtained with nitrogen-shielding from that obtained with argon-shielding. The results obtained with such matrices in this study would strongly support use of such an approach for manganese determinations.

TABLE I.—COMPARISON OF INTERFERENCES FOR MANGANESE DETERMINATION

		Change in signal (%) from 1000, 100 and 10-fold amounts by weight							
		Carbon-filament atom-reservoir						Separated air–acetylene flame	
		AFS*			AAS†			AFS§	
Ion or species	Compound added	1000‡	100‡	10‡	1000‡	100‡	10‡	1000‡	100‡
Al^{3+}	$Al_2(SO_4)_3$	0	0	0	−8	0	0	0	—
Ca^{2+}	$Ca(NO_3)_2$	0	0	0	+30	0	0	0	—
Cr^{3+}	$CrCl_3$	−13	0	0	−70	−67	0	0	—
Fe^{3+}	Fe/HCl	0	0	0	−45	−15	0	0	—
K^+	KNO_3	−10	0	0	−60	−40	0	0	—
Mg^{2+}	$MgCl_2$	−88	0	0	−100	−80	0	−39	−11
Na^+	NaCl	−10	0	0	−40	−20	0	0	—
Ni^{2+}	$Ni(NO_3)_2$	0	0	0	−60	0	0	0	—
Si(IV)	Si/HF	0	0	0	+16	0	0	+5	0
V(IV)	V/HNO_3	−7	0	0	−20	−17	0	+16	8
Cl^-	HCL	0	0	0	0	0	0	0	0
NO_3^-	HNO_3	0	0	0	0	0	0	0	—
PO_4^{3-}	$(NH_4)_2HPO_4$	0	0	0	0	0	0	0	—
SO_4^{2-}	H_2SO_4	0	0	0	0	0	0	0	—

* This study, 5 μl of 0·04 μg/ml manganese solution.
† Ref. 3, 5 μl of 0·4 μg/ml manganese solution.
‡ Weight ratios
§ Ref. 2, 0·5 μg/ml manganese solution.

Effects of foreign ions on AFS of manganese at 279·5 *nm*

The effects of 14 foreign ions on the atomic fluorescence of 5-μl aliquots of 0·04 μg/ml manganese solutions (200 pg) at 1000, 100 and 10-fold weight-ratio levels were studied. An electrodeless discharge lamp was used as the spectral source. Only the fluorescence signal occurring in the range 0–0·7 mm above the rod was viewed, by using a slit fitted in the manner previously described.[3] The effects of these ions are listed in Table I as suppressions or enhancements of the manganese fluorescence signal at 279·5 nm. Only interferences which result in a change of signal of 5% or more were taken to be significant.

It should be noted that at the 10 and 100-fold levels no interference was obtained from any of the ions studied. This would agree with the conclusion reported earlier,[7] that the absolute amount of sample is important, rather than the weight-ratio. The 100-fold level in this study corresponds to a 10-fold amount by weight at the 2-ng level used for absorption studies, at which level no interference with the manganese absorption was reported. At the 1000-fold level interference was observed here for five cations, but only that of magnesium (the most serious interference in flame atomic-fluorescence and non-flame atomic-absorption) was serious. That the other cations studied give less interference in atomic-fluorescence than in atomic-absorption determinations probably results from the higher filament voltage used in the fluorescence measurements and the faster response of the measuring system employed. It was noted that certain oscilloscope traces indicated that effects from elements less volatile than manganese were observed after the manganese signal peak had been passed. Thus with the fast-response system such interferences can be minimized. Advantage might also therefore be expected from the use of this fast-response system to minimize interference in the absorption technique.

TABLE II.—COMPARISON OF DETECTION LIMITS FOR MANGANESE DETERMINATIONS AT 279·5 nm

	Carbon-filament atom-reservoir, *ppm*		Separated air–acetylene flame *ppm**
	5-μl samples	1-μl samples	
Atomic-fluorescence spectroscopy			
(1) with electrodeless discharge lamp source	0·0002† (1 pg)	0·0006† (0·6 pg)	0·001 (2 ng)
(2) with hollow-cathode lamp source	0·001† (5 pg)	0·003† (3 pg)	—
Atomic-absorption spectroscopy			
(1) with electrodeless discharge lamp source	—	—	0·1 (0·2 μg)
(2) with hollow-cathode lamp source	0·01§ (50 pg)	0·03§ (30 pg)	-
(3) with modified d.c. system	0·001§ (5 pg)	0·003§ (3 pg)	—
Flame emission spectroscopy			
(1) at 279·5 nm	—	—	0·05 (0·1 μg)
(2) at 403 nm	—	—	0·01 (20 ng)

* Ref. 2.
† This study
§ Ref. 3.

From this interference study it would appear feasible to improve upon the carbon filament determination of manganese in the presence of elements which interfere in the atomic-absorption technique, by diluting the solution tenfold and then determinating the manganese by atomic-fluorescence spectrometry, provided that a slightly higher coefficient of variation can be tolerated.

CONCLUSION

This study further emphasises the usefulness of the carbon-filament atom-reservoir for the determination of trace metals when only small amounts of sample are available. Table II shows a comparison of the detection limits obtainable in the determination of manganese, when our apparatus is used with an air–acetylene flame and with a carbon-filament atom-reservoir. Either the carbon filament or the flame cell can be used to analyse solutions of the same manganese concentration, but the former requires only 1 or 5 μl of solution whereas the flame cell needs 2 ml of solution. Table I shows that both techniques have good selectivity as well as high sensitivity, and that with the exception of magnesium even at 1000-fold amounts by weight of other ions interfere only slightly when the carbon filament is used in the fluorescence mode.

Acknowledgement—We are grateful to the Procurement Executive, Ministry of Defence, for support of this work.

Zusammenfassung—Es werden die atomischen Fluoreszenzeigenschaften von Mangan, das auf einem KohlenfadenAtomspeicher (CFAR) erhitzt wird, beschrieben, und sie werden mit (a) dem atomischen Absorptionsverhalten des Elements auf dem gleichen Heizfadenapparat, und (b) ihrem Fluoreszenzverhalten in einer getrennten Luft-Acetylenflamme verglichen. Mit Fluoreszenz bei

279,5 nm und 1-μl Mustern kann Mangan mittels einer Lichtquelle elektrodenloser Entladung (3 pg oder 3×10^{-3} ppm durch Absorption und 20 ng oder 1×10^{-2} ppm durch Flammenemission bei 403 pm) bis hinunter auf 0,6 pg (6×10^{-4} ppm) bestimmt werden. Die Wirkungen von vierzehn kennzeichnenden Kationen und Anionen, die untersucht wurden, ergab bei 10-fachen und 100-fachen Stufen keinen störenden Einfluss und ernste Störungseinflüsse von Mangan bei 1000-facher Stufe, mit etwa zehn prozentiger Unterdrückung von Cr, V, Na und K. Es wurden keine Fluoreszenzzeichen ausser bei der Wellenlänge 279,5 nm während Benutzung der CFAR Vorrichtung beobachtet.

Résumé—On décrit les caractéristiques de fluorescence atomique du manganèse chauffé sur un réservoir d'atomes à filament de carbone (CFAR) et les compare avec (a) le comportement d'absorption atomique de l'élément sur le même appareil à filament, et (b) son comportement de fluorescence dans une flamme séparée air-acétylène. Par fluorescence à 279,5 nm, utilisant des échantillons de 1 μl, on peut déterminer le manganèse jusqu'à 0,6 pg (6×10^{-4} p.p.m.) en utilisant comme source une lampe à décharge sans électrode (3 pg ou 3×10^{-3} p.p.m. par absorption, et 20 ng ou 1×10^{-2} p.p.m. par émission de flamme à 403 nm). Les influences de quatorze cations et anions représentatifs examinés ne montrent pas d'interférence à des teneurs 10 et 100 fois supérieures et seul le magnésium apporte une interférence sérieuse à une teneur 1000 fois supérieure, avec une suppression d'environ 10% provenant de Cr, V, Na et K. On n'a observé de signaux de fluorescence à aucune longueur d'onde autre que 279,5 nm lorsque le dispositif CFAR est utilisé.

REFERENCES

1. T. S. West, *Pure Appl. Chem.*, 1971, **25**, 47.
2. L. Ebdon, G. F. Kirkbright and T. S. West, *Talanta*, 1970, **17**, 965.
3. *Idem*, *Anal. Chim. Acta*, 1972, **58**, 39.
4. *Idem*, *ibid.*, in the press.
5. J. Aggett and T. S. West, *ibid*, 1971, **55**, 359.
6. R. G. Anderson, I. S. Maines and T. S. West, *ibid.*, 1970, **51**, 355.
7. D. Alger, R. G. Anderson, I. S. Maines and T. S. West, *ibid.*, 1971, **57**, 271.
8. J. Aggett and T. S. West, *ibid.*, 1971, **57**, 15.
9. M. D. Amos, D. A. Bennett, K. G. Brodie, P. W. Y. Lung and J. P. Matousek, *Anal. Chem.*, 1971, **43**, 211.
10. R. Mavrodineanu and H. Boiteux, *Flame Spectroscopy*. p. 444. Wiley, New York, 1965.

Talanta, 1972, Vol. 19, pp. 1309 to 1320. Pergamon Press. Printed in Northern Ireland

SOME CONSIDERATIONS ON SPECTRAL LINE PROFILES OF MICROWAVE-EXCITED ELECTRODELESS DISCHARGE LAMPS

D. O. COOKE, R. M. DAGNALL and T. S. WEST
Department of Chemistry, Imperial College of Science and Technology, London, SW7

(*Received* 1 *November* 1971. *Accepted* 24 *February* 1972)

Summary—The problems of line broadening in microwave-excited electrodeless discharge lamps for the more volatile elements, P, S, I, Se, Zn, Cd and Hg are discussed in relation to their use in atomic-absorption and fluorescence spectrometry. Both theoretical and practical implications are considered.

THE MICROWAVE-EXCITED electrodeless discharge lamp (EDL) has recently received considerable attention in the literature and it is not surprising that much of this has been concerned with the more volatile elements (As, Se, Hg, Zn and Cd).[1–5] These elements have their main resonance lines in the ultraviolet and generally provide short-lived or less satisfactory hollow-cathode lamps. Furthermore, the detection limits by atomic-fluorescence spectrometry (AFS) for these elements are often a considerable improvement on those obtained for atomic-absorption spectrometry (AAS) provided a suitable high-intensity source (*eg*, an EDL) is used. Recent trends in AAS towards non-dispersive systems, using both interference filters and resonance monochromators[6,7] have also highlighted the importance of the high-intensity source. The resonance monochromator is particularly attractive for routine single element determination when expensive apparatus cannot be justified. Again, this system is particularly well suited to the more volatile elements although with more elaborate apparatus it may be applied to a wider range of elements. Figure 1 shows a spectral scan in the region 200–300 nm, obtained by using such a device for cadmium (simple quartz reservoir with optical flats, maintained at *ca.* 500° in a furnace, with a side-arm to regulate the cadmium vapour pressure at *ca.* 150°). A typical calibration graph obtained by using the device for AAS in conjunction with an EDL and an air–propane flame (circular Méker type burner of path-length *ca.* 2 cm) is included.

The recent interest in non-flame atom reservoirs has enabled very impressive detection limits to be obtained for many of these elements.[8–11] In addition, the advent of such devices has aroused some interest in the direct determination by AAS or AFS of iodine, sulphur and phosphorus.[12] Hitherto the direct determination of these has received little attention. Manning and Slavin,[13] and Kahn *et al.*[14] have examined the determination of phosphorus at non-resonance lines (213·55/213·62 nm and 214·91 nm) and obtained a sensitivity of *ca.* 290 ppm at the 213·55/213·62 lines when using a nitrous oxide–acetylene flame. Although these workers used a hollow-cathode lamp as source, Manning and Slavin mention problems encountered because of the very low intensity and high background associated with the source. In contrast the EDL provides a very high line:background ratio at these wavelengths (Fig. 2) and may prove useful in further improving this type of determination. Thompson[15] has examined the AAS and AFS of iodine at the 206·1 nm non-resonance line, and concluded this to be impracticable; a detection limit of 1·6 mg/ml was obtained by AFS. Using non-flame cells, however, L'vov[12] has obtained sensitivities (for 1 % absorption) in the

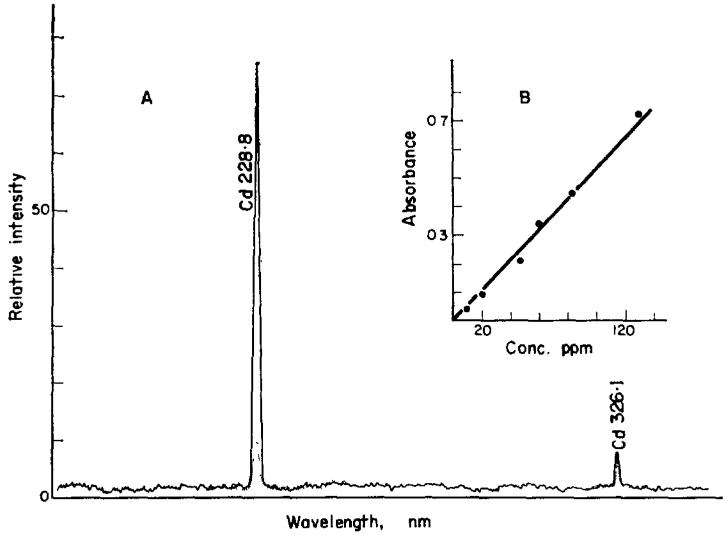


FIG. 1.—(A) Spectral scan of resonance monochromator used in conjunction with Cd EDL; dotted lines indicate the scatter signal (*i.e.*, furnace off).
(B) Calibration curve obtained using the detector in conjunction with air-propane flame; Mêker type burner with path length *ca.* 2 cm.

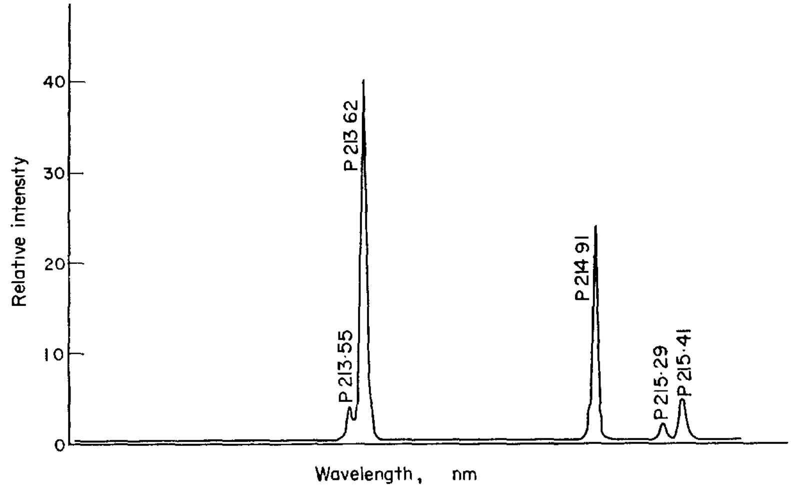


FIG. 2.—Partial emission spectrum of phosphorus EDL; $\frac{3}{4}\lambda$ cavity with microwave power 30 W.

region of 10^{-10}–10^{-12} g for sulphur, phosphorus and iodine, using the main resonance lines in the vacuum ultraviolet region. L'vov used a radiofrequency EDL as source and indeed it would seem that the EDL (radiofrequency or microwave-excited) would be the first choice as spectral source for the resonance lines of such elements. As with the other more volatile elements the main problem in using these EDL's is the critical nature of both preparative and operating conditions. Some idea of the magnitude of the problems involved may be gained from theoretical considerations.

In addition to the natural line width and the Doppler broadening, emission lines from EDL's will be subject to some extent to Lorentz (foreign gas), Holtsmark (resonance) and Stark (electric field) broadening. It seems generally accepted, however that the contribution from Stark broadening, as with Zeeman (magnetic field) broadening, is of little or no significance,[16,17] at least at low total pressures <20 mmHg. Furthermore, the contribution from Doppler broadening is not excessive, because the lamps operate at a relatively low temperature (probably between 400 and 1100°, depending on the microwave power used).

Expressions for the half-intensity line widths (nm) have been given as follows,[10*]

$$\Delta\lambda_N = \frac{\lambda_0^2}{2\pi C} A_{tu} \tag{1}$$

$$= 5{\cdot}32 \times 10^{-19} \lambda_0^2 A_{tu}$$

$$\Delta\lambda_D = \frac{2(2R \ln 2)^{1/2}}{C} \lambda_0 \left(\frac{T}{M_a}\right)^{1/2} \tag{2}$$

$$= 7{\cdot}16 \times 10^{-7} \lambda_0 \left(\frac{T}{M_a}\right)^{1/2}$$

$$\Delta\lambda_L = \frac{2\lambda_0 \sigma_L^2 P_f}{\pi C k T}\left[2\pi R T\left(\frac{1}{M_a} + \frac{1}{M_f}\right)\right]^{1/2} \tag{3}$$

$$= 4{\cdot}67\, \lambda_0^2 \sigma_L^2 P_f 10^{-9} \frac{1}{T}\left(\frac{1}{M_a} + \frac{1}{M_f}\right)^{1/2}$$

$$\Delta\lambda_{\text{Total}} = \{(\Delta\lambda_D)^2 + (\Delta\lambda_L + \Delta\lambda_H + \Delta\lambda_N)^2\}^{1/2} \tag{4}$$

where subscripts N, D and L refer to the natural, Doppler and Lorentz widths respectively, R is the gas constant in erg/mol/K, C is the speed of light in m/sec, T is the absolute temperature, P_f is the pressure of foreign gases in mmHg, M_a is the atomic weight of the absorbing or emitting species in atomic mass units, M_f is the effective (average values for gases) molecular weight of foreign gas molecules in atomic mass units, λ_0 is the wavelength of the line centre in nm, σ_L is the effective cross-section for collisional broadening, A_{tu} is the spontaneous probability between the upper and lower states and k is the Boltzmann constant in erg/K. The value of $\Delta\lambda_H$, the half-intensity width for Holtsmark broadening is obtained from equation (3) by replacing σ_L with σ_H and P_f with P_a, the pressure of absorbing or emitting species, and by replacing M_f with M_a. Ideal gas behaviour is assumed in the derivation of the expressions for $\Delta\lambda_L$ and $\Delta\lambda_H$.[20,21] Table I shows the theoretical half-intensity widths for the resonance lines of certain elements due to natural, Doppler, Lorentz and Holtsmark broadening, together with the total half-intensity widths which have been calculated from equations (1)–(4). The collisional cross-sections are not accurately known and indeed very little information exists regarding optical cross-sections. Winefordner *et al.*[18] have used quenching cross-sections to calculate the half-widths of various absorption lines in flames. The present authors, however, feel that these may lead to somewhat low values. The quenching cross-section for argon is generally assumed to be zero, whilst the optical cross-section for argon at the Na 589·0-nm line has been quoted[22] as 1·12 nm^2 and at the Hg 253·7-nm line as 0·7–0·9 nm^2. Cross-sections for

---

[*] The omission of a factor of 10^{16} in Winefordner's expression has been pointed out by Fassel *et al.*[19]

TABLE I.—EDL EMISSION LINE-WIDTHS FOR VARIOUS ELEMENTS (Theoretical).

	Line *nm*	$\Delta\lambda_N$ Å	Temperature	$\Delta\lambda_D$ Å	$\Delta\lambda_L$, Å		$\Delta\lambda_H$, Å		$\Delta\lambda_T$, Å	
					Max.	Min.	Max.	Min.	Max.	Min.
					$P_f = 7·9$*		$P_a = 15$*			
Cd	228·802	0·000111	500	0·00430	0·00029	0·00003	0·00440	0·00018	0·00645	0·00431
					$P_f = 9·5$		$P_a = 180$			
			650	0·00469	0·00032	0·00004	0·04837	0·00193	0·0490	0·00513
					$P_f = 11·5$		$P_a = 760$			
			850	0·00518	0·00035	0·00004	0·1850	0·00740	0·1856	0·00916
					$P_f = 3$		$P_a = 0·001$†			
Hg	253·652	0·000040	500	0·00357	0·00013	0·00001	Max. 0·0000003		0·00357	0·00357
					$P_f = 3$		$P_a = 0·001$†			
			850	0·00430	0·00011	0·00001	Max. 0·0000002		0·00430	0·00430
					$P_f = 11·5$		$P_a = 760$			
			850	0·00430	0·00041	0·00005	0·17000	0·00680	0·1706	0·00959
					$P_f = 7·9$		$P_a = 40$			
Se	196·026	0·000068	500	0·00439	0·00023	0·00002	0·01039	0·00041	0·01156	0·00442
					$P_f = 9·5$		$P_a = 700$			
			650	0·00480	0·00025	0·00003	0·1647	0·00661	0·1651	0·00825
					$P_f = 7·9$		$P_a = 2$			
Zn	213·856	0·000154	500	0·00527	0·00027	0·00003	0·00067	0·00003	0·00538	0·00527
					$P_f = 9·5$		$P_a = 35$			
			650	0·00576	0·00030	0·00003	0·01078	0·00043	0·01265	0·00579
					$P_f = 11·5$		$P_a = 400$			
			850	0·00635	0·00037	0·00004	0·1117	0·00447	0·1124	0·00788

* Pressures in mmHg.

† Vapour pressure taken as that of Hg at 25° *i.e.*, the situation prevailing in an Hg lamp with reservoir outside the microwave field.

Holtsmark broadening are generally accepted as considerably greater than those for foreign gas species, often as great as 5 nm^2.[22] In view of this uncertainty the line widths have been calculated for maximum and minimum values of the optical cross-sections, *viz* σ_L max 1·5 nm^2, σ_L min 0·5 nm^2, σ_H max 5 nm^2, σ_H min 1 nm.^{2} The lamp parameters assumed are a pressure of argon of 3 mmHg at 20°, and that excess of element is always present, that is, the pressure of the species concerned is given by the vapour pressure at the given temperature (except where stated).

Obviously at the higher pressures, and indeed at all pressures (of emitting species) for which an EDL is likely to be used, there is considerable self-absorption. Very little information exists regarding interferometric measurements of resonance lines emitted by EDL's, although some qualitative results has been reported by Kirkbright and Sargent[23] for calcium and thallium sources (prepared from chlorides). Even with these less volatile species severe self-absorption and self-reversal were observed. L'vov[11] has reported some results for radiofrequency lamps, but they are rather scanty. Typically, he found the line width from a cadmium radiofrequency lamp at 120 mA was equal to that of a hollow-cathode lamp at 10 mA, but the intensity was 1000 times as great. The vapour pressures quoted appear at first sight somewhat high, but although an EDL cannot normally be initiated at a pressure much above 10 mmHg, it is relatively easy to maintain such a discharge up to a pressure of 1 atmosphere. However, even at relatively low pressures the discharge may no longer be homogeneous and self-reversal or quenching of the discharge becomes a problem. The discharge shows a steady transition from the so-called "skin effect" through a homogeneous discharge to that of an arc, under which conditions the resonance lines are severely self-reversed (Fig. 3). A further contribution which has to be taken into account is the shift in wavelength, due to pressure broadening, of both the absorption profile of the analyte atoms and the emission profile of the source ($\Delta\lambda_s$). Theory[24,25] predicts that

$$\frac{\Delta\lambda_S}{\Delta\lambda_C} = -0{\cdot}36 \qquad (5)^*$$

This result yields a red shift which is in agreement with reported results[26,27] for the perturbing species N_2 and Ar, though the values are somewhat lower and 0·25 would appear a more realistic figure. In the case of light perturbing molecules such as H_2, He and Ne, however, the shift can be to the violet. This has recently been explained in terms of the Lindholm theory.[28] It is apparent that a shift of unequal magnitude or in opposing directions, between the emission profile of the source and the absorption profile of the analyte atoms within the atom reservoir, will lead to inferior results in both AAS and AFS. The magnitude of this effect has been evaluated by graphical integration for Gaussian distributions of both emission and absorption profiles and for various emission line widths and wavelength shifts. The results for the case of an absorption line half-width of 2 pm are shown in Fig. 4. The results indicate that for an absorption profile of 2 pm and a shift of *ca* 0·5–0·6 pm and a source line width of 0·45 pm and a shift of *ca.* 0·05–0·2 pm (see Table I, *e.g.* Cd EDL at 500°), the separation $\Delta\lambda_{sp}$ (of peak wavelengths of the absorption and emission profiles) would be *ca.* 0·3–0·55 pm and the absorption signal would be depressed by *ca.* 2–4%. The situation is more pronounced at larger emission line widths, but in these instances it should be remembered that the signal is already degraded because the ratio of emission line width to absorption line width (α) is no longer $\ll 1$. For example, in the case of an

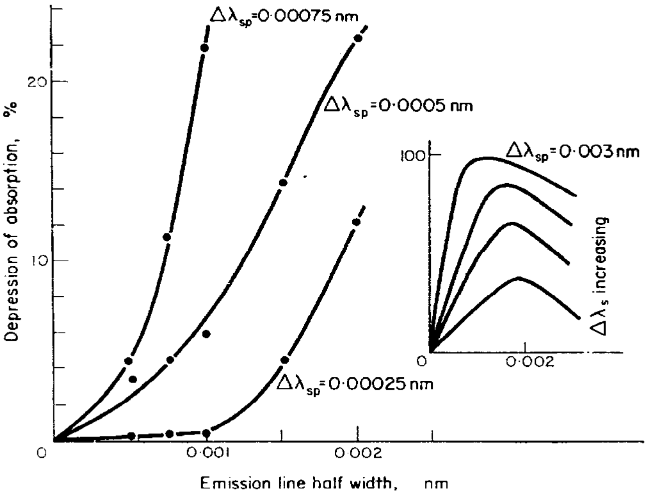


FIG. 4.—Depression in absorption for various wavelength shifts and emission line widths; absorption line width assumed to be 0·002 nm.

---

* Although the ratio $\Delta\lambda_S/\Delta\lambda_C$ is zero for the C_3/r^3 term of Lindholm's expression the van der Waals term C_6/r^6 is dependent on the total pressure of all uncharged species.

absorption profile of 2 pm width and a shift of *ca.* 0·5–0·6 pm and a source broadened to a line width of 2 pm, (as might be the case for a Cd EDL at 500°), whilst the shift remains *ca.* 0·05–0·2 pm the already degraded absorption would be further depressed by *ca.* 20–30% relative to that which would result from a zero shift in the absorption profile.

Hyperfine structure (*hfs*)[30]

The presence of hfs in a spectral line (a result of the radiating atoms consisting of a mixture of isotopes or of possessing a non-zero nuclear spin) also contributes to an increase in line width and to a decrease in analytical signal (in AAS) in addition to that predicted from theoretical considerations.[21] The presence of hfs in a spectral line is analogous to the situation arising when more than one transition falls within the spectral bandpass of the monochromator.[29,34] The deviation from the theoretical growth curve for peak absorption due to the presence of hfs is somewhat complex and varies with the element (and isotope ratios) concerned. Evidence at present suggests its effect to be significant. Model calculations[29] in the case of copper have indicated a decrease of 16% in sensitivity due to the presence of hfs, whilst decreases considerably in excess of this could well be expected. However, the presence of hfs has been neglected in the line-width calculations concerned in this study.

Such is the magnitude of line broadening, self-absorption and the shift in wavelength when an EDL is used under adverse circumstances, that they may be qualitatively observed by using a conventional (prism) monochromator when operating in the far ultraviolet. Figure 5 shows a series of spectral scans of the selenium 196·026 nm line at various microwave power levels and illustrates clearly the effects of self-absorption. It is not expected that any self-reversal present would be resolved. Unlike EDL's for many elements, the selenium lamp shows little tendency towards arc formation even at very high pressures. Figure 6 shows spectral scans of the selenium 196·026 nm line with and without *ca.* 50,000 ppm of selenium nebulized into the flame (the high concentration was necessary because of gross broadening present in the source). The shift in wavelength between the absorption profile and the source emission profile may just be observed. The bismuth 195·948 nm emission line was

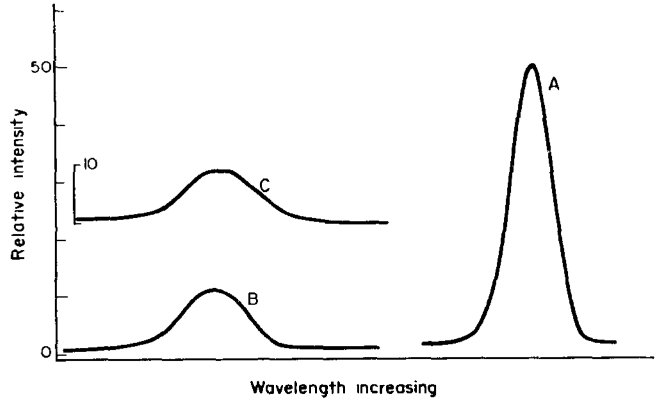


FIG. 5.—Spectral scans of Se 196·026 line at various microwave powers; scan-rate 0·8 nm/min, spectral slit <0·005 nm, lamp (Se metal/argon) operated in $\frac{3}{4}\lambda$ cavity. (A) 50 W; (B) 150 W; (C) 180 W

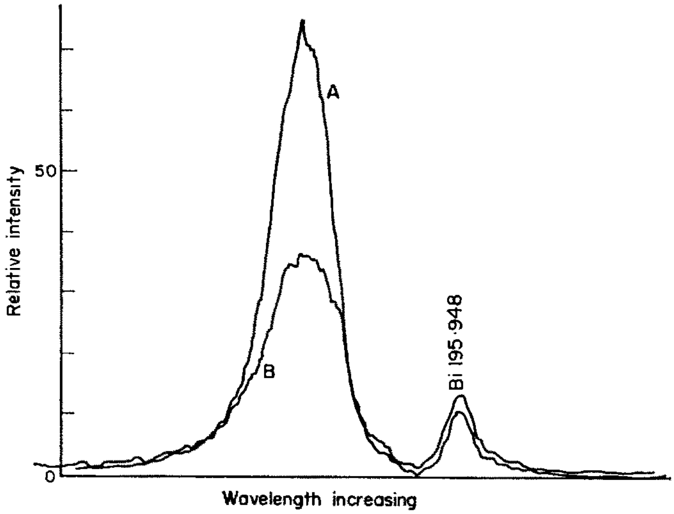


FIG. 6.—Spectral scans of Se 196·026 nm line at 150 W, other conditions as for Fig. 5. (A) after passage through flame; (B) on nebulizing *ca.* 50,000 ppm Se.

obtained by using a separate EDL as a wavelength guide to facilitate alignment of the individually recorded spectra. It is of interest, however, that the absorption profile appears to be shifted to a longer wavelength than that of the source. The shift of absorption profile in the flame, from equation (5) would be expected to be *ca.* 0·85–0·5 pm and any shift to a longer wavelength in the source would reduce the separation. The observation of this separation may well suggest that the source line profile has shifted towards the violet. Attempts to observe a shift in wavelength for the bismuth line were unsuccessful, though in this instance the emission line would not be as readily broadened as the selenium emission.

Practical implications

The practical consequences of the ease with which emission lines from EDL's may be broadened or reversed may be considered in two distinct aspects.

Those applications for which line broadening is advantageous. Into this class falls the technique of line overlap which has received particular attention in AFS and more recently in AAS. Such occurrences have been recognized for some time as a source of spectral interference in AAS.[19] The importance of line broadening in this technique is readily appreciated, owing to the separation which already exists between the absorption and emission profiles. There are three reasons for the use of line overlap methods. First, under certain circumstances they permit improved sensitivities in AFS as a result of an effective higher line intensity from the line overlap source as opposed to the more normal source. Such occurrences are, however, rare and so far as the authors are aware increased sensitivity has so far only been obtained in the case of the determination of bismuth at 206·170 nm, using the iodine 206·163 nm emission line.[31] Secondly, to provide an increased range for a given source. Several workers have reported examples,[32,33,34] although sensitivities in AAS (or absolute signal in AFS) are invariably lower than those which are obtained when using the more conventional source. Frank *et al.*[35] have determined Mg, Mn, Ni and Cu, using an iron hollow-cathode lamp. Fulton *et al.*[36] have examined the AFS of cadmium (228·802 nm), using the arsenic (228·812 nm) non-resonance line and obtained a detection limit of 0·0017 ppm, a factor of only 3 below that more normally obtained by using the same premixed flame (air–acetylene) and a cadmium EDL.[37] The line separation in this instance is (+) 0·01 nm which would be further removed from the absorption line profile by any shift in wavelength of the arsenic 228·812 nm line. The third reason for the use of line overlap procedures, perhaps at first sight rather surprising, is to enable a reduction in sensitivity to be obtained when the more normal methods, such as burner rotation, sample dilution or the use of a less sensitive line are not possible. As yet this has only been reported for calcium.[38]

Those applications for which line broadening is detrimental. The requirement of a narrow emission line width in AAS (ratio of emission line width to absorption line $\alpha \ll 1$) is well known.[12,21] Deviation from this requirement will result in decreased absorbance values and departure from linearity of the calibration curve.* In AFS, however, line width is of less importance because the presence of unwanted radiation outside the absorption profile has little or no effect on the analytical signal. Gross broadening such that the emission line is effectively a continuum over the absorption line profile will of course result in a change in shape of the growth curve[39,40] at high concentration. However, this effect is difficult to observe before severe self-absorption or self-reversal of the emission line (which leads to a decrease in intensity at the line centre or over the whole absorption profile) results in a decreased analytical signal. The importance of the EDL line widths as regards the analytical situation may be seen from Table II which shows the theoretical line widths for various elements under various analytical conditions. Calculations in this instance have excluded any contribution due to resonance broadening because in an analytical useful situation this is negligible in comparison with other causes of line broadening. Comparison of Tables I and II indicates that α is by no means always $\ll 1$. The situation appears particularly critical when the sources are used in conjunction with low temperature operation of a non-flame cell, under which circumstances non-linearity in AAS would be expected. The use of a high-pressure device appears at first sight to rectify this, but the shift of the absorption profile would lead to a decrease in sensitivity relative to that which could be obtained by improving the source conditions.

Obviously then, to ensure optimal results for an EDL prepared from volatile elements, it must be ensured that the pressure within the EDL is maintained as low as possible. A particularly attractive, though often difficult, means of ensuring these conditions, is to use the quantity of material within the lamp as the vapour pressure regulator.[41] Provided sufficiently small amounts of material are introduced into the lamp, the sensitivity in AAS, and under certain circumstances the AFS signal, may be increased. Table III shows some sensitivities obtained when using various zinc EDL's.

---

* It should be noted that even when the so-called ideal source is used there is some decrease in atomic absorbance from the theoretical peak absorption (apart from considerations relating to hyperfine structure) due to the shift in absorption profile of the analyte atoms in the flame or other atom reservoir. A truly ideal source would therefore have an emission line shifted in wavelength by the same amount as that of the absorption profile whilst still maintaining the condition $\alpha \ll 1$. Clearly from equation (5), this is not likely to be a practical occurrence.

The reader is reminded of the other causes of curvature of calibration curves, namely chemical interferences (ionization, compound formation) and the non-linear relation between flame gas concentration and solution concentration, due to variation in nebulization efficiency.

TABLE II.—ABSORPTION LINE WIDTHS FOR VARIOUS ANALYTICAL CONDITIONS (Theoretical).

	Line *nm*	Atom reservoir	Temperature, °*C*	$\Delta\lambda_D$, Å	$\Delta\lambda_L$, Å		$\Delta\lambda_T$, Å	
					Max.	Min.	Max.	Min.
Cd	228·802	A	2207	0·0080	0·0308	0·0019	0·0319	0·0082
		B	800	0·0051	0·0235	0·0026	0·0242	0·0057
		C	1400	0·0063	0·0188	0·0020	0·0199	0·0066
		D	1400	0·0063	0·0944	0·0105	0·0947	0·0124
		E	700	0·0048	0·0244	0·0027	0·0250	0·0056
Hg	253·652	A	2207	0·0064	0·0360	0·0022	0·0366	0·0067
		B	800	0·0042	0·0272	0·0029	0·0276	0·0051
		C	1400	0·0052	0·0219	0·0024	0·0226	0·0057
		D	1400	0·0052	0·1092	0·0121	0·1092	0·0128
Se	196·026	A	2207	0·0079	0·0235	0·0015	0·0249	0·0080
		B	800	0·0052	0·0182	0·0019	0·0190	0·0055
		C	1400	0·0065	0·0146	0·0016	0·0160	0·0067
		D	1400	0·0065	0·0731	0·0081	0·0734	0·0104

A Slightly fuel-rich air–acetylene flame.[18] $M_t = 29{\cdot}77\sigma_c$ max $= 2{\cdot}0$ nm; σ_c min $= 0{\cdot}5$ nm.

B,C CFAR[8,46] argon at 1 atmosphere.

D L'vov furnace, [11,12] argon at 5 atmospheres.

E Above a microwave-excited argon plasma, using a platinum loop device.[47,48]

TABLE III.—SENSITIVITIES* (ppm for 1% absorption) AT 213·8 nm USING VARIOUS ZINC EDL'S.

Lamp	Microwave power 20 W	30 W	40 W	50 W	60 W
5 μg $ZnCl_2$	—	—	0·136	0·095	0·078
20 μg $ZnCl_2$	0·081	0·055	0·050	0·057	0·095
100 μg $ZnCl_2$	0·050	0·136	0·110	—	—
<100 μg Zn	0·078	0·110	0·122	0·120	—
>2000 μg Zn	0·122	0·136	0·157	0·157	—

* Air–propane flame (*ca* 10 cm). Lamps prepared with 3 mmHg argon pressure and operated in a three-quarter wave cavity.

Zinc chloride lamps have been included because in this instance the effect is somewhat more pronounced (presumably due to the presence of free chlorine) and may be more readily examined. Much of the discussion here is of course applicable to EDL's prepared from volatile compounds, with the additional problems that the secondary constituent (normally a halogen) affords an increase in total pressure within the lamp. This may be an important problem if the constituents do not recombine readily on cooling. Furthermore, the collisional cross-sections for the halogens are appreciably greater than that for argon[22] and thus additional broadening can result from halogen present within the lamp. For very volatile elements with sufficient vapour pressure for operation at room temperature, long lamps, having a reservoir of the element (or compound) well outside the microwave field (which can be maintained at room temperature or cooled if necessary) can prove useful. The authors have operated such lamps some 20–25 cm long for mercury and iodine. The discharge does not fill the lamp, but it is normally advantageous to enable the discharge to come into contact with the top of the lamp as this tends to improve stability. A carrier-gas pressure of *ca.* 1–3 mmHg is normally required to ensure initiation of such a discharge and is essential in the case of iodine. Small diameter (2 mm bore instead of the more normal 8 mm) lamps used under these conditions can sometimes be useful, owing to a further reduction in self-absorption.

When the vapour pressure at room temperature is insufficient to provide a high intensity in long lamps, *e.g*, sulphur, zinc, then slightly larger lamp dimensions than normal (*i.e.*, >3 cm length) can provide a useful improvement in signal, although only at the expense of stability and warm-up time. It is best to ensure that the discharge fills the lamp, or migration of material to the much cooler portion will result in a considerably reduced radiation output. Cooling of the lamp may also be an advantage, but unless the air flow is accurately regulated, poor stability will result. Cooling of a lamp can seldom result in greater improvement than that which may be readily obtained by other means (reduction of microwave power or modification of preparative conditions).[46] The carrier gas normally chosen is argon, although the other inert gases have all been examined.[12,42,43] In addition to the problem of short lifetime when helium is used, the somewhat higher temperature of operation associated with helium lamps renders its choice undesirable for volatile species. The use of helium or neon could possibly be expected to induce shift in emission profile opposing that of the absorption profile in the atom reservoir. However, in view of the low pressure of carrier gas involved it is considered that this is likely to be of little consequence. Sensitivities obtained in AAS when using helium and argon-filled lamps are generally similar, provided both can be optimized with respect to microwave power (Table IV).

TABLE IV.—SENSITIVITIES* (ppm for 1% absorption) AT 213·8 nm USING VARIOUS ZINC EDL'S

Carrier-gas†	Carrier-gas pressure, *mmHg*	Microwave power, *W*	Sensitivity, *ppm*
Argon	1	31	0·111
Argon	3	33	0·114
Argon	5	32	0·108
Argon	8	23	0·120
Helium	1	21	0·120
Helium	2	21	0·120
Helium	4	18	0·116

* Air–propane flame (*ca* 10 cm).

† Lamps prepared using excess zinc metal and operated in a three-quarter wave cavity.

Because of the comparatively insignificant contribution to line broadening afforded by the carrier gas (Table I), variation of this parameter can also provide a useful means of improving the analytical signal. This would appear to be a result of the decreased operating temperature of lamps containing higher pressures of argon. Figure 7 shows the effect of argon pressure on the AAS of zinc. As can be seen the rate of decrease in absorbance at high microwave powers increases as the pressure is decreased. The highest absorbance is obtained at *ca.* 5 mmHg. Lamps prepared with argon pressures of ≤1 mmHg were comparatively short-lived (10–50 hr), although they could be initiated on heating the lamp. Line: background ratios were high in all

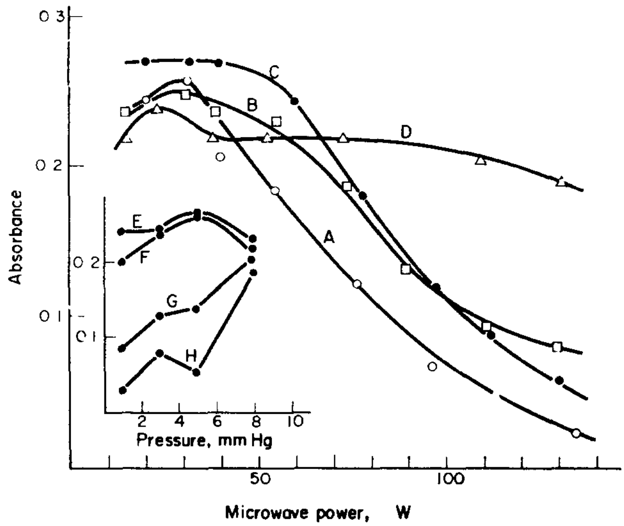


FIG. 7.—Effect of microwave power on AAS of zinc; nebulizing 5 ppm zinc solution, and using EDL's prepared at various argon pressures.
(A) 1 mmHg; (B) 3 mmHg; (C) 5 mmHg; (D) 8 mmHg; (E) 20 W; (F) 50 W; (G) 90 W; (H) 130 W

instances, ranging between 100:1 and 2000:1, depending on the lamp and its operating conditions. Optimum AAS performance was normally obtained at line:background ratios of 100:1–300:1. The effect of argon pressure on the AFS signal is more markedly dependent on the properties of the element or compound concerned than for AAS. For example, a decrease in argon pressure (down to 0·5 mmHg) results in an increase in AFS signal for zinc lamps (made with zinc metal); this was the lowest pressure at which the discharge could be initiated readily. However, some improvement at higher pressures may be obtained for very highly volatile elements when self-absorption/self-reversal is particularly pronounced; in certain instances higher pressure may provide a higher line intensity and an increased sensitivity in AFS for less volatile species such as Tl[44] and Mn.[43]

Acknowledgements—We thank Beckman-RIIC Ltd. for the provision of a research grant to one of us (DOC) and for the loan of some of the apparatus used in this study.

Zusammenfassung—Die Probleme der Verbreiterung der Linien in elektrodenlosen, Mikrowellen erregten Entladungslampen werden für die flüchtigeren Elemente P, S, I, Se, Zn, Cd und Hg in Bezug auf ihre Verwendung in Atomabsorption und Fluoreszenzspektrometrie besprochen. Es werden sowohl theoretische wie praktische Begleiterscheinungen in Betracht gezogen.

Résumé—On discute du problème de l'élargissement des raies dans les lampes à décharge sans électrode excitées par micro-ondes pour les éléments les plus volatils, P, S, I, Se, Zn, Cd et Hg, en relation avec leur emploi en spectrométrie d'absorption atomique et de fluorescence. On considère les conséquences tant théoriques que pratiques.

REFERENCES

1. R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1968, **15**, 677.
2. *Idem.*, *ibid.*, 1967, **14**, 557.

3. R. F. Browner, R. M. Dagnall and T. S. West, *ibid.*, 1969, **16,** 75.
4. M. S. Cresser and T. S. West, *Anal. Chim. Acta*, 1970, **50,** 517.
5. G. B. Marshall and T. S. West, *ibid.*, 1970, **51,** 179.
6. J. V. Sullivan and A. Walsh, *Spectrochim. Acta*, 1966, **22,** 1843.
7. A. Walsh, *Pure Appl. Chem.*, 1970, **23,** 1.
8. J. F. Alder and T. S. West, *Anal. Chim. Acta*, 1970, **51,** 365.
9. J. R. Mislan, *At. Energy Can. Ltd.*, No. 1941, 1964.
10. H. Massmann, *Spectrochim. Acta*, 1968, **23B,** 215.
11. B. V. L'vov, *ibid.*, 1970, **24B,** 53.
12. *Idem*, *Atomic Absorption Spectrochemical Analysis*, Hilger, London, 1970.
13. D. C. Manning and S. Slavin, *At. Abs. Newslett.*, 1969, **8,** 132.
14. J. D. Kerber, W. B. Barnett and H. L. Kahn, *ibid.*, 1970, **9,** 139.
15. K. C. Thompson, *Spec. Lett.*, 1970, **3,** 59.
16. S. Tolansky, *High Resolution Spectroscopy*, 1st Ed., Methuen, London, 1947.
17. C. F. Bruce and P. Hannaford, *Spectrochim. Acta*, 1971, **26B,** 207.
18. M. L. Parsons, W. J. McCarthy and J. D. Winefordner, *Appl. Spectry.*, 1966, **20,** 223.
19. V. A. Fassel, J. O. Rasmuson and T. G. Cowley, *Spectrochim. Acta*, 1968, **23B,** 579.
20. R. G. Breene, Jr., *The Shift and Shape of Spectral Lines*, Pergamon, New York, 1961.
21. A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, London, 1961.
22. H. G. Kuhn, *Atomic Spectra*, 2nd Ed. Longmans, London, 1969.
23. G. F. Kirkbright and M. Sargent, *Spectrochim. Acta*, 1970, **25B,** 577.
24. W. Lenz, *Z. Physik*, 1933, **80,** 423.
25. E. Lindholm, *Arkiv. Mat. Astron. Fysik.*, 1946, **32A,** No. 17.
26. S. Ch'en and M. Takeo, *Rev. Mod. Phys.*, 1957, **29,** 20.
27. T. Hollander, B. J. Jansen, J. J. Plaat and C. Th. J. Alkemade, *J. Quant. Spectry. Radiative Transfer*, 1970, **10,** 1301.
28. W. Behemenburg and H. Kohn, 1964, **4,** 163.
29. Z. v. Gelder, *Spectrochim. Acta*, 1970, **25B,** 669.
30. S. Tolansky, *Hyperfine Structure in Line Spectra and Nuclear Spin*, 2nd Ed., London, 1948.
31. R. M. Dagnall, K. C. Thompson and T. S. West, *Talanta*, 1967, **14,** 1467.
32. D. C. Manning and F. Fernandez, *At. Abs. Newslett.*, 1968, **7,** 24.
33. D. C. Manning, *ibid.*, 1967, **6,** 75.
34. G. L. Vidale, *Gen. Elec. Tech. Inform. Service Rept.*, No. R605D330.
35. C. W. Frank, W. G. Schrenk and C. E. Meloan, *Anal. Chem.*, 1966, **38,** 1005.
36. A. Fulton, K. C. Thompson and T. S. West, *Anal. Chim. Acta*, 1970, **51,** 373.
37. R. S. Hobbs, *Ph.D. Thesis*, London, 1971.
38. K. C. Thompson, *Analyst*, 1970, **95,** 1043.
39. H. P. Hooymayers, *Spectrochim. Acta*, 1968, **23B,** 567.
40. P. J. Th. Zeegers and J. D. Winefordner, *ibid.*, 1971, **26B,** 161.
41. D. O. Cooke, R. M. Dagnall and T. S. West, *Anal. Chim. Acta*, 1971, **54,** 381.
42. W. E. Bell, A. L. Bloom and J. Lynch, *Rev. Sci. Instr.*, 1961, **32,** 688.
43. M. D. Silvester and W. J. McCarthy, *Spectrochim. Acta*, 1970, **25B,** 229.
44. D. O. Cooke, R. M. Dagnall and T. S. West, *Anal. Chim. Acta*, 1971, **56,** 17.
45. L. de Galan and G. F. Samuey, *Spectrochim. Acta*, 1969, **24B,** 679.
46. T. S. West and X. K. Williams, *Anal. Chim. Acta*, 1969, **45,** 27.
47. M. P. Bratzel, Jr., R. M. Dagnall and J. D. Winefordner, *ibid.*, 1969, **48,** 197.
48. A. Cummings, R. M. Dagnall and B. L. Sharp, unpublished work.

Talanta, 1972, Vol. 19, pp. 1321 to 1334. Pergamon Press. Printed in Northern Ireland

CONTROLLED POTENTIAL COULOMETRY: THE APPLICATION OF A SECONDARY REACTION TO THE DETERMINATION OF PLUTONIUM AND URANIUM AT A SOLID ELECTRODE

J. B. FARDON and I. R. MCGOWAN
British Nuclear Fuels Ltd., Windscale and Calder Works, Sellafield, Seascale
Cumberland, U.K.

(*Received* 6 *September* 1971. *Accepted* 6 *March* 1972)

Summary—A method is described for the simultaneous determination of plutonium and uranium in mixed oxides by controlled potential coulometry at a gold working electrode in two stages: first a coulometric oxidation, at 0·73 V *vs.* a silver/silver chloride electrode, of Pu(III) and U(IV) to Pu(IV) and U(VI) by a combination of a direct electrode reaction and a secondary chemical reaction proceeding concurrently, and secondly, a coulometric reduction at 0·33 V of Pu(IV) to Pu(III), leaving uranium as U(VI). The determination is carried out in a mixture of sulphuric and nitric acids, and Ti(III) is used to reduce plutonium and uranium to Pu(III) and U(IV) before electrolysis. The precision (3σ) of Pu:U ratio results obtained from mixtures containing about 30% and 2% plutonium was 0·5% and 1·5% respectively. The effect of experimental variables on the time taken to complete the coulometric determination is discussed.

THE FABRICATION of mixed oxide fuel for both thermal and fast reactors has led to a substantial analytical requirement for the determination of plutonium and uranium in oxides containing approximately 2–30% plutonium. In order to extend the range of techniques available for this purpose, it was decided to attempt the development of a coulometric method.

There are well-established methods for the individual determination of these elements by controlled potential coulometry, *e.g.*, plutonium by electrolysis at a platinum or gold electrode,[1] and uranium at a mercury pool electrode.[2] A difficulty in the way of a method suitable for the determination of both elements is the large difference in the potentials of the redox couples involved. Electrolytic reduction of uranium(VI) to uranium(IV) in dilute mineral acid requires a more negative potential than can normally be obtained at a platinum or gold electrode without simultaneous reduction of hydrogen ion. Advantage is therefore taken of the high hydrogen overvoltage on mercury. However, the more positive potentials required for plutonium coulometry in mineral acid media would oxidize mercury, and a noble metal must be chosen in this case.

Thus the determination of plutonium and uranium by coulometry normally involves two entirely distinct measurements in separate cells equipped with the appropriate working electrodes. It would obviously be beneficial, in terms of convenience and economy, to be able to carry out both determinations in a single procedure.

The formal potential of the plutonium(IV)/(III) couple may be lowered by working with a citrate medium so that a mercury electrode may be used for the determination[3] but in this medium the formal potentials of the uranium and plutonium couples are not sufficiently different to allow both elements to be determined separately. Uranium has been determined by reduction at a silver electrode[4] without the concurrent liberation of hydrogen, but this electrode is unlikely to be suitable for use at the potentials required for the plutonium electrolysis. The evolution of hydrogen at a platinum electrode has been overcome by using constant-current potential limit coulometry[5] with addition of bismuth(III) to the electrolyte and periodically anodizing the electrode. Under these conditions plutonium and uranium were determined successively at a platinum electrode with a relative standard deviation of ±0·2% for each element.

In developing the new method described in this paper, consideration was first given to the redox process that might be employed. A conventional coulometric procedure for the determination of plutonium[6] in which a redox cycle between the tervalent and quadrivalent states is carried out by electrolysis at a noble metal electrode in a sulphuric acid medium was chosen as the basis for development. The attractive features of the method are as follows.

(*a*) Plutonium can be determined without interference from uranium(VI).

(*b*) The presence of nitric acid in the electrolyte can be tolerated, thus nitric acid used to dissolve mixed oxide would not have to be removed from the solution.

(*c*) It has been demonstrated[1] that the time required for electrolysis can be shortened considerably by using a gold electrode with a large surface area.

It was estimated that it would be possible to determine the sum of plutonium and uranium by coulometric oxidation provided that these elements were initially present as plutonium(III) and uranium(IV). Despite the much lower formal potential of the uranium(IV)/(VI) couple, uranium(IV) is not electroactive at the potential required for quantitative oxidation of plutonium(III). However, the mechanism envisaged was electrolytic production of plutonium(IV), which would oxidize uranium(IV) to give uranium(VI), and the regenerated plutonium(III) would again undergo electrolytic oxidation until eventually both plutonium and uranium were fully oxidized to the quadrivalent and sexivalent states, respectively.

This proposal requires that the two elements should initially be present as plutonium(III) and uranium(IV). An all-electrolytic process would present the basic problem of conflicting requirements for electrode materials. It appeared that this problem could be circumvented by the use of a chemical reduction treatment to avoid the need for mercury cathode electrolysis. However, it would be essential to have a sure method for destruction of the excess of reductant without oxidizing any of the uranium(IV) or plutonium(III). Titanium(III) in a mixture of sulphuric and nitric acids was chosen as the reductant on the ground that the solution medium would be compatible with the coulometric oxidation stage proposed for the determination of the sum of plutonium and uranium.

The new method was designed on the basis of these concepts, which are amplified in the next section. Since the method depends on the secondary reaction between uranium(IV) and plutonium(IV), information on the factors which govern the rate of this reaction is included, together with a brief review of the published uses of secondary reactions in coulometry. This paper covers experimental work carried out to develop a satisfactory procedure for mixtures containing more than 2% plutonium, and to determine its performance characteristics.

SECONDARY REACTIONS IN CONTROLLED POTENTIAL COULOMETRY

Various authors have referred to secondary reactions occurring during controlled-potential coulometric analysis. Meites and Moros[8] in a review of factors which contribute to the magnitude of background-current corrections in coulometry have defined a kinetic quantity of electricity which results from cyclic processes involving the oxidation and reduction of products of the primary electrode reaction. The effect is illustrated by the reduction of vanadium(IV) inducing the reduction of hydrogen ions. Geske and Bard[9] have presented a mathematical treatment of various hypothetical reaction schemes in which secondary chemical reactions occur which generate or consume the electroactive material, and methods of calculating the *n*-value of complex secondary reactions are described. Coulometric measurements have been used to calculate the kinetics of secondary reactions. For example Rechnitz and McLure[10] have studied the kinetics of the iridium(III)/chlorate reaction, using steady-state controlled-potential coulometry in the presence of excess of chlorate, and McCullough and Meites[11] have described the disproportionation of the product, and the chemical interaction between reactant and product during the coulometric reduction of niobium(V). An example of an analytical application is provided by the work of Shults[12] on a secondary coulometric method for the determination of plutonium by reducing plutonium(VI) with electrogenerated iron(II). This method was designed to overcome the interfering effect of iron on the normal procedure for the determination of plutonium.

No method appears to have been published in which a secondary reaction is used to determine two species quantitatively, one species being electroactive and the other not. For the determination of plutonium and uranium the following procedure was envisaged.

(*a*) Chemical treatment of the sample to convert it quantitatively into plutonium (III) and uranium(IV).

(*b*) Coulometric oxidation of plutonium(III) to (IV) concurrently with which the chemical reaction between plutonium(IV) and uranium(IV) would occur, forming uranium(VI) and regenerating plutonium(III).

(*c*) Continuing step (*b*) until the final products of the coulometric oxidation are uranium(VI) and plutonium(IV). The integrated current measured would correspond to the two-electron oxidation of uranium and the one-electron oxidation of plutonium.

(*d*) Coulometric reduction of plutonium(IV) to (III) under conditions where uranium(VI) remains stable. The integrated current for this step would correspond to plutonium alone.

i.e.,

$$\begin{array}{lll}
\mathrm{Pu(III)} & \rightarrow \mathrm{Pu(IV)} & \text{Electro-oxidation} \\
\mathrm{Pu(IV)} + \mathrm{U(IV)} & \rightarrow \mathrm{Pu(III)} + \mathrm{U(VI)} & \text{Chemical reaction} \\
\mathrm{Pu(III)} + \mathrm{U(IV)} & \rightarrow \mathrm{Pu(IV)} + \mathrm{U(VI)} & \text{Complete electro-oxidation} \\
\mathrm{Pu(IV)} & \rightarrow \mathrm{Pu(III)} & \text{Electro-reduction}
\end{array}$$

Information has been published on the conditions suitable for the chemical reduction [step (*a*)]. In the redox titration method described by Corpel and Regnaud[13] plutonium and uranium are reduced to the ter- and quadrivalent states respectively by titanium(III) in a mixture of nitric, sulphuric and sulphamic acids. This medium would be suitable for the coulometric procedure, and the reduction system has the additional advantage that a pre-electrolysis step could be carried out before the plutonium is electrolysed to ensure that all of the titanium is in the quadrivalent state.

It was expected that the efficiency of steps (*b*) and (*c*) would be influenced by the rate of the chemical reaction between uranium(IV) and plutonium(IV). The kinetics of this reaction in perchlorate solution have been studied by Newton[14] who showed that the rate was first-order with respect to uranium(IV) and plutonium (IV) and inversely proportional to the square of the hydrogen-ion concentration. The presence of traces of sulphuric acid accelerated the reaction. More recent work on perchloric acid solutions[15] has shown rates 3–5 times faster than those reported by Newton, and rates in nitric acid about half those in perchloric acid. The reaction rate has been considered during assessment of the suitability of uranium(IV) as an alternative reductant to iron(II) in nuclear-fuel reprocessing plants,[16] and it was concluded that the reaction was sufficiently fast in the aqueous phase to allow complete reduction of plutonium(IV) in solvent extraction equipment giving mixing times of 1–2 min. Although the conditions existing in a reprocessing plant, namely the provision of a concentration of uranium(IV) greater than that stoichiometrically equivalent to the plutonium(IV), would be different from those expected for the present application, it was felt that the reaction between uranium(IV) and plutonium(IV) during the coulometric oxidation would not be inconveniently slow, particularly since as the oxidation approaches completion the plutonium(IV) concentration would approach its maximum value.

EXPERIMENTAL

Apparatus

The controlled-potential coulometer used in this work was similar to that described by Goode *et al.*[2] The integrated current readings were made with a digital voltmeter, Dynamco type DM 2001 Mk. 2. The coulometer was calibrated electrically by substituting precision resistors for the electrolysis cell, following standard practice. The electrical calibration in coulombs per volt was converted into weight of plutonium or uranium per volt by using Faraday's laws.

The electrolysis cell comprised a flat-bottomed glass vessel 35 mm in diameter and 70 mm high, fitted with a polythene stopper (Fig. 1). Through the stopper were inserted two Corning 7930 Vycor unfired glass tubes of ¼ in. diameter, one containing a silver/silver chloride, saturated potassium chloride reference electrode, and the other containing a platinum wire spiral, both in $0{\cdot}5M$ sulphuric acid. The reference electrode sheath was made by plugging a length of polythene tubing, 3 mm bore and 1 mm wall thickness, with a short length of Vycor rod. The cell also contained a glass stirrer, having a paddle in the form of a disc with corrugations, driven by a 24-V d.c. motor capable of approximately 6000 rpm, and a tube to provide an argon purge. The gold working electrode comprised two pieces of 48-mesh expanded sheet, each 2 × 72 cm, spot-welded to a length of 16 S.W.G.

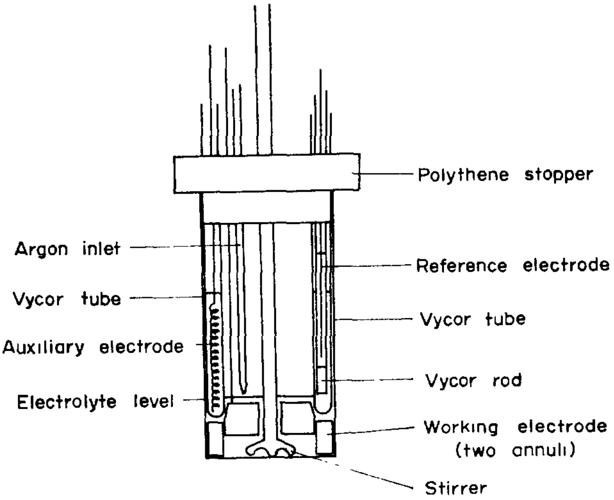


FIG. 1.—Coulometer cell.

gold wire to provide an electrical connection. Each was coiled so as to provide two ring electrodes, one of which would fit partly inside the other.

Reagents

Solutions were prepared by dissolving plutonium–uranium mixed oxides in $8M$ nitric acid/$0{\cdot}05M$ hydrofluoric acid, evaporating to remove the excess of fluoride and then diluting with $1M$ nitric acid to give a total metal concentration of 20–30 mg/ml.

Titanium(III) sulphate solution was prepared by refluxing a mixture of 50 ml of water, 10 ml of concentrated sulphuric acid and 5 g of titanium sponge, until the metal had dissolved. The solution was stored over a piece of cadmium metal in an atmosphere of argon.

Procedure

Transfer the sample solution containing 15–20 mg of plutonium plus uranium to the titration cell, together with 5 ml of a $0{\cdot}25M$ sulphuric–$1M$ nitric acid mixture and 1 ml of saturated sulphamic acid solution. Set the stirrer at approximately 500 rpm and direct the argon flow over the surface of the electrolyte. Add titanium(III) solution dropwise until present in excess, as judged by a darkening in colour of the electrolyte. Allow the chemical treatment to proceed for 10 min. Increase the stirrer speed to approximately 5000 rpm and pre-electrolyse the solution at a potential of 0·33 V *vs.* silver/silver chloride until the electrolysis current falls to 20 μA or less. Apply a potential of 0·73 V *vs.* silver/silver chloride to the working electrode and electrolyse until the current falls to a low and constant value of 25 μA or less. The integrated current for this process corresponds to the oxidation of the plutonium(III) to (IV) and the uranium(IV) to (VI). Determine the plutonium by applying a voltage of 0·33 V to the working electrode and electrolysing until the current falls to a low and constant value of about 10 μA or less. Correct the integrated current at both analytical voltages for integrator drift and residual current by the standard procedure.

Carry out a blank determination using the same quantity of reagents but with the plutonium–uranium solution omitted.

Subtract the corrected integrated current readings for the blank from the corresponding readings for the sample at the two voltages, and calculate the weights of uranium and plutonium in the sample from the electrical calibration of the coulometer.

RESULTS

Preliminary investigation

The selection of the working electrode potentials required did not present any difficulty since those normally used for the determination of plutonium in a sulphuric acid medium would apply. The method chosen for the chemical treatment of the sample to produce uranium(IV) and plutonium(III) did not require any change to be made to the electrode potentials. In the chemical treatment the titanium(III) reduces the uranium and plutonium and the excess of titanium(III) is oxidized by the nitric acid present[13] in the electrolyte. A pre-electrolysis at 0·33 V *vs.* silver/silver chloride, which would normally be carried out for a plutonium determination, was also found to be suitable to oxidize any remaining titanium(III). After the 10-min reaction time allowed in the procedure, pre-electrolysis normally required only 2–3 min and the integrated current was usually very small. It did, however, ensure that a reproducible starting point was achieved before each run.

The procedure was tested on a pure plutonium standard. The results obtained did not differ significantly from those obtained when the plutonium was determined in sulphuric acid electrolyte containing neither nitric acid nor titanium. A precision (3σ) of $\pm 0{\cdot}4\%$ with no detectable bias was obtained on 6-mg quantities of plutonium. Solutions containing both plutonium and uranium were analysed and the results were compared with those obtained by amperometric redox titration methods in which the plutonium was determined by reduction from plutonium(VI) to (IV) in sulphuric acid by iron,[17] and uranium by the oxidation of uranium(IV) to (VI) in phosphoric–sulphuric acids by dichromate.[18] Results are shown in Table I.

TABLE I.—RESULTS FOR PLUTONIUM AND URANIUM BY COULOMETRY AND REDOX TITRATION.

Method	Plutonium, *mg/ml*	Uranium, *mg/ml*	Ratio, 100 × Pu/(Pu + U)
Coulometry	$2{\cdot}86_3$, $2{\cdot}85_7$	15·55, 15·54	$15{\cdot}5_5$, $15{\cdot}6_1$
Redox titration	$2{\cdot}86_3$	15·54	$15{\cdot}5_8$
Coulometry	$4{\cdot}98_1$, $4{\cdot}99_4$	12·44, 12·46	$28{\cdot}5_9$, $28{\cdot}6_1$
Redox titration	$5{\cdot}00_1$	12·44	$28{\cdot}6_6$

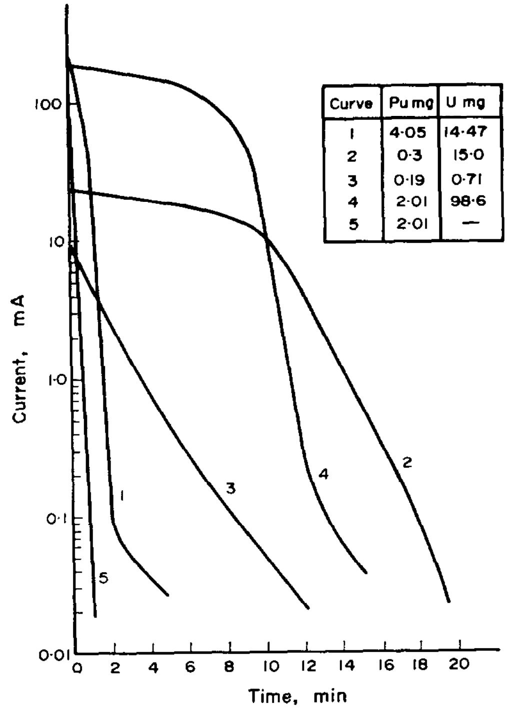
With the large surface-area gold electrode the coulometric oxidation of plutonium (III) and uranium(IV) [which includes the secondary reaction between plutonium(IV) and uranium(IV)] at 0·73 V *vs.* silver/silver chloride was complete in 5–6 min and the coulometric reduction of plutonium alone required 2 min. However, when solutions of low plutonium–uranium ratio were analysed, the time for the oxidation was increased to about 20 min for samples containing 15–20 mg of plutonium and uranium. It became apparent that with solutions of low plutonium–uranium ratio (about 5%) the rate of oxidation was controlled by a rate-limiting process, presumably either the rate of generation of plutonium(IV) at the working electrode or the rate of the chemical reaction between plutonium(IV) and uranium(IV). The rate of the electrode reaction is influenced primarily by the cell parameters, that is by the size of the working electrode, the volume of electrolyte and efficiency of stirring, whilst the rate of the chemical reaction is enhanced by increase in the concentration of plutonium(IV) and uranium (IV), and by decrease in the concentration of acid.

In controlled-potential coulometry where a single electrode reaction occurs under limiting current conditions the overall effective constant k is given in the expression $i_t = i_0\, e^{-kt}$ where i_0 and i_t are the current at time zero and t. Figure 2 shows current–time curves for plutonium and plutonium–uranium mixtures. Curve 5 corresponds to the electrolysis of 2 mg of plutonium, and from this curve a value for k of 0·07 sec^{-1} was calculated. This value is in good agreement with others reported for high-speed coulometry.[1,7] When plutonium–uranium solutions were analysed, the shape of the current–time curves depended on the plutonium–uranium ratio of the sample and the total quality of plutonium and uranium in the cell. Examples are discussed below.

Emphasis was placed on obtaining optimum conditions for a rapid coulometric oxidation step for two reasons, first to reduce the overall time for the determination of plutonium and uranium to a minimum in the interests of analytical convenience and economy, and secondly, because the corrections (due to residual current and integrator drift) to be applied to the integrated current reading for the electrolysis are smaller the shorter the electrolysis time.

The determination of plutonium and uranium

High plutonium–uranium ratio. For analysis of solutions of high plutonium–uranium ratio (greater than about 15%), the time required for the electrolytic oxidation was approximately the same as that for solutions of pure plutonium in quantities that gave an equivalent total integrated current. Curve 1 in Fig. 2 shows the current–time characteristics of a mixture containing 4·05 mg of plutonium and 14·47 mg of uranium, [Pu/(Pu + U) = 21·9%)]. The rate of the reaction was found to be unaffected by a small variation in the acidity of the electrolyte or plutonium and uranium concentration. When the concentrations of uranium and plutonium were decreased



Curve	Pu mg	U mg
1	4·05	14·47
2	0·3	15·0
3	0·19	0·71
4	2·01	98·6
5	2·01	—

FIG. 2.—Current-time curves for plutonium and plutonium–uranium mixtures.

markedly but the same plutonium–uranium ratio was maintained, the electrolysis time was increased and a negative bias appeared in the result. This effect is illustrated by curve 3 in Fig. 2, where 0·19 mg of plutonium and 0·71 mg of uranium were electrolysed [Pu/(Pu + U) = 21·9 %]. The electrolysis of less than 1 mg of plutonium would be expected to be complete within 1 min (*cf.* curve 5). The plutonium–uranium ratios calculated from the determinations corresponding to curves 1 and 3 were 21·9 % and 21·4 % respectively.

Solutions prepared from sintered plutonium–uranium mixed oxides were analysed by the coulometric procedure, and the results were compared with those obtained by redox titration and by X-ray spectrometry. These results are shown in Table II. For coulometry, samples containing 15–20 mg of plutonium plus uranium were used.

The agreement between these results is good, especially in view of fundamental differences in the character of the methods. The X-ray method, for example, is wholly dependent upon the integrity of the plutonium–uranium standards used for its calibration, whereas the coulometry results were calculated from the electrical calibration of the coulometer and were independent of plutonium–uranium standards.

TABLE II.—PLUTONIUM–URANIUM RATIO RESULTS ON MIXED OXIDES.

Coulometry			Redox titration	X-Ray spectrometry
100 × Pu/(Pu + U) Mean	Precision (3σ) %	Number of determinations	100 × Pu/(Pu + U)	100 × Pu/(Pu + U)
$15{\cdot}5_6$	0·8	11	$15{\cdot}5_6$	—
$23{\cdot}9_4$	0·7	10	$23{\cdot}9_8$	$23{\cdot}9_5$
$28{\cdot}6_2$	0·5	10	$28{\cdot}6_6$	$28{\cdot}5_9$

Low plutonium–uranium ratio. Current-time curves for samples of low plutonium–uranium ratio are illustrated for a 2% mixture in Fig. 2, curves 2 and 4. A comparison of curves 1 and 2 which represent samples of similar plutonium plus uranium content, and hence similar integrated currents for the oxidation process, shows the effect of plutonium–uranium ratio on the electrolysis time. When a series of solutions containing about 2% plutonium was analysed by the procedure described, that is with a sample of about 15 mg of plutonium plus uranium, the results showed a poor precision ($3\sigma = 4{\cdot}7\%$) and also a negative bias of about 2% when compared with results from the redox titration and X-ray spectrometry methods. The negative bias was shown to be related to the effect already noted on high plutonium–uranium ratio samples, by varying the quantity of plutonium plus uranium in the cell. It was found that as the size of the sample was increased from 15 to 100 mg the bias disappeared and also the time for the electrolysis to be completed was reduced (*cf.* curves 2 and 4 in Fig. 2). Accurate results were obtained when the sample contained more than about 1 mg of plutonium. With low plutonium–uranium ratio samples this resulted in relatively large quantities of uranium in the cell, but as shown by curve 4, Fig. 2, the overall coulometric oxidation was completed within a convenient time. An improvement in precision for low plutonium–uranium ratio results was obtained by modifying the basic procedure. It follows that since uranium(VI) does not interfere with the normal coulometric method for the determination of plutonium by reduction and oxidation of the plutonium(IV)–(III) couple, the plutonium may be determined first before titanium(III) is added to reduce the sample to plutonium(III) and uranium(IV). The recommended modification to the basic procedure is as follows.

Transfer a portion of the sample solution containing 1–2 mg of plutonium to the titration cell together with 5 ml of a 0·25*M* sulphuric–1*M* nitric acid mixture and 1 ml of saturated sulphamic acid solution.

Set the stirrer at approximately 5000 rpm and purge with argon for 5 min. Pre-electrolyse the solution at 0·33 V *vs.* silver/silver chloride until the current falls to about 10 μA. Zero the integrator then apply a potential of 0·73 V and electrolyse until the current falls to about 10 μA. The integrated current for this step corresponds to the oxidation of plutonium(III) to (IV).

Proceed with the addition of titanium(III) and carry out the basic procedure.

More precise results for plutonium were obtained by using this modification, and so the precision of the plutonium–uranium ratio was improved. The improvement was brought about primarily by the effect of the modification on the size and precision of the titration blank. When the modified procedure was used, the blank correction amounted to 2·0% of the integrated current for the electrolysis of 2 mg of plutonium, and the precision (3σ) of the blank calculated from results accumulated over several weeks was 22·2%. The lower limit imposed by the blank on the precision attainable for the plutonium determination was thus 0·45%. When the determination was carried out as described in the experimental section, that is on less than 0·5 mg of plutonium for a 2% plutonium sample, and plutonium was determined after the coulometric oxidation step, the precision of the blank limited the precision attainable for the plutonium determination to about 3% (3σ).

In the modified procedure developed specifically for the analysis of low plutonium–uranium ratio samples, the time required for the coulometric oxidation step was not affected by small changes in the plutonium or uranium concentration or in the acidity of the medium. The results obtained on four different solutions prepared from plutonium–uranium mixed oxides are shown in Table III.

TABLE III.—PLUTONIUM–URANIUM RATIO RESULTS ON MIXED OXIDES.

Sample	Coulometry 100 × Pu/(Pu + U)	X-Ray spectrometry 100 × Pu/(Pu + U)
1	$1\cdot99_7$	$1\cdot99_6$
2	$1\cdot55_9$	$1\cdot55_9$
3	$1\cdot80_6$, $1\cdot82_5$, $1\cdot82_4$ $1\cdot80_2$, $1\cdot82_3$	$1\cdot81_3$
4	$1\cdot80_4$, $1\cdot80_6$, $1\cdot79_6$ $1\cdot79_7$, $1\cdot79_8$	$1\cdot80_5$

The precision of the coulometric method is 1·5% (3σ) at this level, and the bias between the coulometric and X-ray spectrometry results is insignificant. The time taken for the coulometric oxidation step in these samples was about 15 min, and the plutonium determination required less than 2 min.

Maintenance of the working electrode

For the determination of plutonium and uranium a large surface-area gold electrode was chosen to ensure a high rate of electrolysis and thus a short analysis time. For analysis of pure plutonium solutions an occasional cleaning by immersion in chromic acid sufficed to keep the working electrode in good condition. With plutonium–uranium solutions it was more important that the electrode should be treated with chromic acid daily to maintain high initial electrolysis currents and short titration times. This effect is presumably related to the strong reducing treatment which the electrode is subjected to during the chemical reduction of the sample with titanium(III). Although it would be possible to reduce the sample and then introduce the electrodes after the excess of titanium(III) had been oxidized by the nitric acid, it was considered more convenient to carry out all steps in the procedure directly in the titration cell. The first run carried out each day was usually found to be anomalous in either the result obtained or the titration time, probably because of adsorption of chromic acid, and for this reason two or three blanks were normally run first to ensure reproducibility of the cell conditions. This type of behaviour is frequently encountered in coulometric work and in electrometric titration end-point detection systems. When not in use the electrode was stored in chromic acid.

Interferences

At an early stage in this work a coulometer cell was used in which the reference electrode comprised a silver/silver chloride electrode in saturated potassium chloride in a Vycor tube, which was immersed directly in the electrolyte. It was found that chloride diffusing through the Vycor tube adversely affected the precision of the results, particularly with low plutonium–uranium ratio samples. The diffusion of chloride into the electrolyte was greatly reduced with a reference electrode having the design shown in Fig. 1. The tip of the reference electrode is plugged with a short length of Vycor rod, which has a much lower leakage rate than Vycor tube, and the electrode is enclosed in a Vycor tube containing $0\cdot5M$ sulphuric acid. It is likely that the chloride affected the reproducibility of behaviour of the gold working electrode. Fluoride on the other hand did not interfere in the quantities present from the dissolution of samples of mixed oxides in $8M$ nitric acid–$0\cdot05M$ hydrofluoric acid. Some of this fluoride would be lost during dissolution, but when the sample taken comprised 0·5 ml of the acid mixture, the result for the plutonium–uranium ratio agreed with that obtained from a second portion of the sample which had been treated with a few drops of sulphuric acid and evaporated to fumes of sulphur trioxide to remove fluoride. Iron was found to interfere quantitatively with the result for plutonium, but not with uranium. Iron is likely to be the major metal impurity in mixed oxides, and the effect of other impurities at much lower concentrations would not be significant.

DISCUSSION

Throughout this work emphasis was placed on establishing conditions such that the coulometric/chemical oxidation of plutonium(III) and uranium(IV) should proceed rapidly and quantitatively so that the overall time for the determination might be reduced to a minimum. This involved optimizing both the rate of electrolysis and the rate of the chemical reaction. The former was shown to compare favourably with other reported high-speed coulometric studies. Rechnitz[10] has reviewed the conditions which must be fulfilled in order to determine the rate of a secondary chemical reaction proceeding in opposition to a primary electrode reaction. This author has determined the rate constant for the second-order reaction between iridium(III), electrogenerated from iridium(IV), and chlorate, having established conditions where a steady state existed, *i.e.*, the rates of the electrode reaction and the chemical reaction were the same. This condition was manifested by the appearance of a constant electrolysis current following the initial exponential decay which is expected in controlled-potential coulometry. Because of the slowness of the iridium–chlorate reaction[10] ($k = 1{\cdot}92 \times 10^{-2}$ l.mole^{-1}min^{-1} the electrolysis current had decayed appreciably before the onset of a constant current, and furthermore the concentration of chlorate did not change appreciably as a result of the chemical reaction. In the present work the secondary reaction between plutonium(IV) and uranium(IV) obviously proceeded very rapidly. Although some of the current-time curves exhibited a plateau, no evidence was found for a decay in current occurring before the plateau was established, as would be expected if the rate of regeneration of plutonium(III) by chemical reaction were rate-limiting. In addition, the oxidation of uranium(IV) was obviously proceeding rapidly in the plateau region. Newton[14] has reported that the second-order rate constant for the uranium(IV)–plutonium(IV) reaction is $5{\cdot}3 \times 10^2$ l.mole^{-1}.min^{-1} in $2M$ perchloric acid at 20°. The addition of a trace of sulphuric acid ($2 \times 10^{-3}M$) increased the rate of reaction by a factor of about 50.

Some rate measurements on the reaction between plutonium(IV) and uranium(IV) were made in the present work. The conditions were by no means rigorously controlled, and the observations served only to establish approximately the rate under the experimental conditions used for the coulometric analysis. The reaction was carried out in the titration cell by adding known amounts of plutonium(IV) to a solution of uranium(IV) which had been formed by the titanium(III) reduction procedure. After varying intervals of reaction time, the residual plutonium(IV) was determined by coulometric reduction to plutonium(III). Errors would be introduced by this measurement technique because of the finite time required for the reduction of the plutonium (IV), but by choosing conditions where the residual plutonium(IV) concentration was small, the majority of it was reduced within the first few seconds of electrolysis. The measurements were carried out in a mixture of $0{\cdot}5M$ sulphuric–$1M$ nitric acids, with

4 mg of plutonium and 2–6 mg of uranium, and a second-order rate constant of about 2×10^5 l.mole^{-1}.min^{-1} was obtained. This reaction rate is approaching the theoretical maximum value measurable for secondary chemical reactions by steady-state coulometry with a high-speed titration cell.[10] It was concluded therefore that any limitation in the rate of coulometric oxidation of plutonium(III) and uranium(IV) in the present application resulted from the electrode reaction generating plutonium(IV). This observation is supported by two further factors.

(*a*) A short appraisal had been made of the suitability of a coulometric cell having a small-area platinum working electrode to be used in conjunction with a potentiostat having a limited current-handling capacity. The platinum electrode cell produced initial electrolysis currents of about 50 mA in comparison with 250 mA or greater from the gold cell when used for the coulometric oxidation of plutonium and uranium. Table IV shows results obtained, using both of these cells, for the time taken to attain a residual current of 25 μA or less when analysing samples of high and low plutonium–uranium ratio.

TABLE IV.—COMPARISON OF PLATINUM AND GOLD WORKING ELECTRODE CELLS.

Working electrode	Time to reach a residual current of <25 μA, *min*		100 × Pu/(Pu + U)
	Coulometric oxidation of plutonium + uranium	Coulometric reduction of plutonium	
Large gold	5	2	$21{\cdot}9_0$
	5	2	$21{\cdot}8_7$
Small platinum	14	5	$21{\cdot}8_6$
	13	6	$21{\cdot}7_7$
Large gold	15	1	$2{\cdot}0_7$
Small platinum	Only 65 % complete after 25 min		

These results confirm that the time for the overall oxidation of plutonium(III) and uranium(IV) is very dependent upon the electrolysis cell parameters and consequently upon the rate of electrogeneration of plutonium(IV). The design of stirrer and speed of rotation used in the present work are not usual in controlled-potential coulometry, but the arrangement was found to give smoother and more efficient stirring than a conventional paddle at slower speeds in the present application.

(*b*) The importance of apparatus and equipment design was exemplified further by primary coulometric reactions carried out on large quantities of sample. In Fig. 2, curve 4 represents the oxidation of about 100 mg of plutonium plus uranium. The integrated current for this oxidation is equivalent to that from the oxidation of about 200 mg of plutonium. Because of experimental difficulties associated with handling 200 mg of plutonium in the cell, the measurement of a current–time curve for this quantity of sample was not possible, but iron may be oxidized and reduced under similar conditions to plutonium in a sulphuric acid electrolyte and was used as a convenient alternative. The current–time curve obtained for 48 mg of iron, which is equivalent in integrated current to about 206 mg of plutonium, is shown in Fig. 3. Its characteristics are very similar to those of curve 4, Fig. 2, confirming that the exponential decay of electrolysis current obtained with small samples does not hold when determining large samples with the same cell design.

It was concluded that the chosen electrolyte was a suitable medium for a rapid chemical reaction during the coulometric oxidation of mixtures of plutonium(III) and

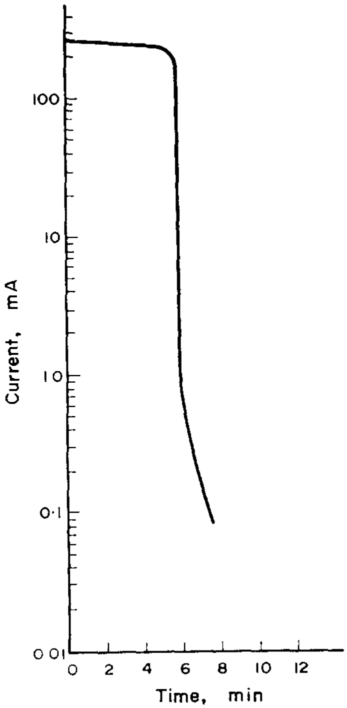


FIG. 3.—Current-time curve for iron (48 mg).

uranium(IV). It was advisable on principle to limit the amount of acid added in the sample to be analysed, but no differences were found in the plutonium–uranium ratio results or the titration time when the acidity of the sample was equivalent to 1 ml of 4*M* or 1 ml of 1*M* nitric acid. As an alternative to the use of titanium(III) as reductant for the chemical pretreatment of the plutonium–uranium sample, the use of electrolysis at a mercury pool was considered. This procedure would have the advantages that the addition of extraneous metal ions would be avoided, it could be carried out directly in sulphuric–nitric acid mixtures, and it would be possible to electro-deposit iron, the major interference in the plutonium determination. It would have the disadvantage, however, of greater complexity of apparatus and manipulations involved, and there would be uncertainty associated with quantitative transfer of sample to the coulometer cell and ensuring that no oxidation of the plutonium(III)–uranium(IV) mixture occurred during transfer.

A general advantage of the ability to determine both plutonium and uranium by one analysis in a single sample is that when only the plutonium–uranium ratio is required, no elaborate sample handling is needed. An accurate weight of plutonium–uranium mixed oxide need not be taken for analysis, nor need the sample be transferred quantitatively to the titration cell. For the coulometric method it is necessary to ensure only that the sample contains about 15 mg of plutonium plus uranium for high plutonium–uranium ratios, and about 100 mg for low ratios, the significant point being that the sample should contain at least 1 mg of plutonium.

The controlled potential coulometric procedure for the determination of plutonium and uranium is to the authors' knowledge the first reported procedure in which two major components in a mixture are determined quantitatively by a sequence of the type $A \rightarrow B$, $B + C \rightarrow D + A$ where A and B are electroactive and C and D are not at the potentials used. Reported work which is similar in principle has not been designed to achieve quantitative reaction of both components. The application is not restricted to plutonium and uranium. Iron may be used instead of plutonium so that the determination of uranium may be carried out conveniently in sulphuric/nitric acids at a solid electrode. This procedure may have advantages over the conventional determination at a mercury pool in some circumstances, *e.g.*, with a large solid electrode it is likely to be faster if a favourable iron–plutonium ratio is used, even though the method would be a two-stage procedure. In addition the determination would be more tolerant to nitric acid than the mercury pool method, and might be less prone to error from interferences, *e.g.*, ruthenium, which lowers the overvoltage for hydrogen evolution at mercury.

Zusammenfassung—Es wird ein Verfahren zur gleichzeitigen Bestimmung von Plutonium und Uranium in Mischoxyden durch geregelte Potentialcoulombmessung an einer goldenen Betriebselektrode in zwei Stufen beschrieben: erstens eine coulombmetrische Oxydierung bei 0,73 V versus einer Silber/Silberchloridelektrode von Pu(III) und U(IV) auf Pu(IV) und U(VI) durch eine Kombinierung einer direkten Elektrodenreaktion und einer gleichzeitig erfolgenden, sekundären chemischen Reaktion, und zweitens, eine coulombmetrische Reduktion von Pu(IV) auf Pu(III) bei 0,33 V, die Uranium als U(VI) hinterlässt. Die Bestimmung wird in einer Mischung von Schwefel- und Stickstoffsalzen durchgeführt und Ti(III) wird zur Reduktion von Plutonium und Uranium auf Pu(III) und U(IV) vor Elektrolyse benutzt. Die Genauigkeit (3σ) der Ergebnisses des Pu:U Verhältnisses, das sich aus Mischungen mit 30% und 2% Plutonium ergab, war 0,5% bzw. 1,5%. Die Wirkung experimenteller Veränderlichen auf die beanspruchte Zeit zur Beendigung der coulombmetrischen Bestimmung wird besprochen.

Résumé—On décrit une méthode pour le dosage simultané du plutonium et de l'uranium dans des oxydes mixtes par coulométrie à potentiel contrôlé en deux stades sur une électrode de travail en or: d'abord une oxydation coulométrique, à 0,73 V par rapport à une électrode argent/chlorure d'argent, de Pu(III) et U(IV) en Pu(IV) et U(VI) par une combinaison d'une réaction directe à l'électrode et d'une réaction chimique secondaire se développant concuremment, puis une réduction coulométrique à 0,33 V de Pu(IV) en Pu(III), laissant l'uranium à l'état U(VI). Le dosage est mené dans un mélange d'acides sulfurique et nitrique, et Ti(III) est utilisé pour réduire le plutonium et l'uranium en Pu(III) et U(IV) avant électrolyse. La précision (3σ) des résultats des rapports Pu:U obtenue à partir de mélanges contenant environ 30% et 2% de plutonium a été de 0,5% et 1,5% respectivement. On discute de l'influence de variables expérimentales sur le temps nécessaire pour réaliser le dosage coulométrique.

REFERENCES

1. G. C. Goode and J. Herrington, *Anal. Chim. Acta*, 1965, **33**, 413.
2. G. C. Goode, J. Herrington and G. Hall, *ibid.*, 1964, **30**, 109.
3. F. A. Scott and R. M. Peekema, *Proc. U.N. Intern. Conf. Peaceful Uses At. Energy*, 1958, **28**, 573.
4. G. W. C. Milner and J. W. Edwards, *U.K. At. Energy Authority, Res. Group Rep.*, R 3951.
5. V. M. Sinclair, W. Davies and J. L. Drummond, *U.K. At. Energy Authority, T.R.G. Report* 1165 (D).
6. W. D. Shults, *Talanta*, 1963, **10**, 833.
7. A. J. Bard, *Anal. Chem.*, 1963, **35**, 1125.
8. L. Meites and S. A. Moros, *ibid.*, 1959, **31**, 23.

9. D. H. Geske and A. J. Bard, *J. Phys. Chem.*, 1959, **63**, 1057.
10. G. A. Rechnitz and J. E. McLure, *Anal. Chem.*, 1964, **36**, 2265.
11. J. G. McCullough and L. Meites, *J. Electroanalyt. Chem.*, 1968, **19**, 111.
12. W. D. Shults, *Anal. Chem.*, 1961, **33**, 15.
13. J. Corpel and F. Regnaud, *Anal. Chim. Acta*, 1962, **27**, 36.
14. T. W. Newton, *J. Phys. Chem.*, 1959, **63**, 1493.
15. P. Biddle, J. H. Miles and M. J. Waterman, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1736.
16. A. Naylor, *U.K. At. Energy Authority*, *Prod. Group*, *P.G. Report* 817(W).
17. J. Cherry, J. Holmes and J. J. B. Williams, *ibid.*, 832(W).
18. J. Cherry, *ibid.*, 827(W).

Talanta, 1972, Vol. 19, pp. 1335 to 1348. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF PLUTONIUM AND URANIUM IN MIXED OXIDE FUELS BY SEQUENTIAL REDOX TITRATION

P. H. CHADWICK and I. R. MCGOWAN
British Nuclear Fuels Limited, Windscale and Calder Works, Sellafield, Seascale, Cumberland, U.K.

(*Received* 6 *September* 1971. *Accepted* 6 *March* 1972)

Summary—The use of a sequential determination of uranium and plutonium in a single sample solution results in a saving in analysis time and apparatus requirements. The method starts with U(IV) and Pu(III) in a mixture of sulphuric and nitric acids. Titration with dichromate, using amperometry at a pair of polarizable electrodes, produces two well-defined end-points corresponding to the sequential oxidation of U(IV) to U(VI) and Pu(III) to Pu(IV). The quantitative oxidation of U(IV) to U(VI) is achieved *via* the action of Pu(IV) as intermediate, and is dependent upon establishing conditions which favour rapid reaction between U(IV) and Pu(IV). The method is precise and accurate. With Pu-U mixtures containing between 15 and 30% plutonium the precision (3σ) of the Pu:U ratio results is ±0·6% on samples containing 100–120 mg of plutonium plus uranium. Iron and vanadium interfere quantitatively with plutonium, copper interferes non-quantitatively with uranium, and gross amounts of molybdenum mask the uranium end-point.

REDOX TITRATION methods are widely used for the determination of plutonium and uranium in plutonium–uranium mixed oxides. The methods in use for this purpose fall into two categories.

(*a*) Methods for the determination of plutonium where uranium does not interfere, and for uranium where plutonium does not interfere. The results from two separate determinations thus give the required information on the mixed oxide. Such methods are typified by those developed at D.E.R.E.; plutonium was determined, by Drummond and Grant,[1] by potentiometric titration of plutonium(VI) with iron(II) in a mixture of sulphuric and nitric acids, and uranium, by Davies and Gray,[2] by the oxidation of uranium(IV) to (VI) in phosphoric acid with dichromate to an end-point indicated by a redox indicator. Variations on these methods, in which amperometric end-point detection is used,[3,4] are in regular routine use at Windscale.

(*b*) Methods in which one of the variations in (*a*) is used in conjunction with a method which determines total plutonium plus uranium. An example is that described by Waterbury *et al.*[5] in which plutonium alone is determined by reduction of plutonium(VI) without interference from uranium, and the plutonium plus uranium, by cerimetric oxidation of plutonium(III) and uranium(IV) in a mixture of hydrochloric and sulphuric acids. A similar approach has been described by von Baeckmann *et al.*[6] Again the results of two separate determinations give the information required.

A saving in time and effort and a reduction in the number of facilities required would result from a method capable of determining plutonium and uranium sequentially in one sample. In principle the formal potentials of the plutonium(IV)–(III) and uranium(VI)–(IV) couples are sufficiently different for a sequential determination of the two elements by oxidation or reduction titrations to be considered. The difficulty in obtaining a reliable sequential determination by oxidation is probably associated with slowness in attainment of equilibrium during the oxidative titration of uranium(IV) to uranium(VI), since the analysis of pure uranium solutions is frequently carried out by adding an excess of dichromate to oxidize the uranium(IV) and back-titrating the remaining excess with a reductant after a waiting period,[7] or by adding an excess of iron(III) and titrating the iron(II) formed, with an oxidant.[9] It is significant, however, that uranium(IV) may be titrated directly with standard iron(III) solution, and good titration curves are obtained provided that favourable solution conditions and end-point detection methods are selected. Thus Florence and Shirvington[10] titrated uranium(IV) in 0·2*M* sulphuric acid at room temperature and recommended the use of amperometry with a dropping mercury electrode. The low-acid medium was chosen because it enhanced the rate of the uranium(IV)–iron(III) reaction, the rate being inversely proportional to the square of the acid concentration.[10,11] Since the formal potentials of the iron(III)–(II) and plutonium(IV)–(III) couples are very similar in sulphuric acid solution it was thought that acidity would be an important factor in the sequential oxidation of uranium(IV) and plutonium(III). This paper shows that plutonium(IV) behaves as an oxidizing intermediate during the titration of uranium(IV) and plutonium(III) with dichromate, and that the quantitative determination of uranium is strongly influenced by the acidity of the titration medium. Dichromate was used as oxidant because it is a reliable widely used standard; it is stable in water and therefore suitable for maintaining low-acid titration conditions. The chemical conversion of samples into the uranium(IV) and plutonium(III) oxidation states was achieved by the titanium(III) reduction method in sulphuric–nitric acids[8] for its convenience, reliability and tolerance to nitric acid, the latter point being a desirable feature because this acid is commonly used for dissolving mixed oxides. Both potentiometric and amperometric indication of equivalence points were investigated.

Under the conditions described, two equivalence points, corresponding to the quantitative oxidation of uranium(IV) to (VI) and plutonium(III) to (IV), are detected with high sensitivity. The method is suitable for the determination of plutonium and uranium in mixed oxides having compositions encountered in fast-reactor fuels, and the results produced are free from bias as judged by the analysis of plutonium–uranium standards.

EXPERIMENTAL

Apparatus

Titrations were carried out in a 100-ml beaker equipped with a glass stirrer driven by a 6-V d.c. motor. Dichromate solutions were delivered from either a glass burette (10-ml, A grade), or a polythene weight burette. The weight burettes were made from 2-oz polythene bottles by sealing a polythene tube with a fine tip to the neck of each bottle. An Agla micrometer syringe (0·5 ml capacity) was used for the precise location of end-points.

Potentiometric measurements were made with a calomel electrode and a platinum foil electrode (Type EPT 23, Electronic Instruments Ltd.) approximately 1 cm square. The potential was measured with a Pye Dynacap pH meter. For constant-current potentiometry, two EPT 23 electrodes were used, polarized by current supplied by a 90-V battery connected through a suitable megohm resistor (Fig. 1).

The amperometric indicator circuit employed the same two platinum electrodes connected to a 1·5-V battery through a 1000-ohm potentiometer and 2200-ohm fixed resistor. The potential applied

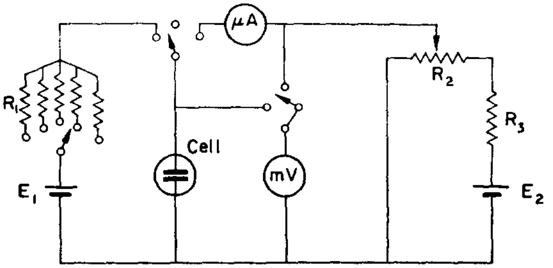


FIG. 1.—Polarizing circuit.

$E_1 = 90$ V $E_2 = 1{\cdot}5$ V
R_1 = various fixed resistances, 3·6–45 MΩ
$R_2 = 1{,}000\ \Omega$ $R_3 = 2{,}200\ \Omega$

across the electrodes was varied by adjusting the potentiometer, and measured with the pH meter. The indicator current was measured with a Cambridge spot galvanometer having a sensitivity of 12 scale divisions per μA (Fig. 1).

The electrodes were cleaned before use by immersion in chromic acid.

Materials

Uranium(VI) nitrate standard solution. Reactor-grade uranium dioxide with known total impurities was heated in air to U_3O_8. A known weight of the U_3O_8 was dissolved in 8*M* nitric acid, and the solution was diluted to 2*N* acidity to provide a weight standard (about 150 mg/g, 200 mg/ml).

Plutonium(IV) nitrate standard solution. A purified plutonium nitrate solution was assayed by igniting weighed aliquots in air at 1250° and weighing as stoichiometric plutonium dioxide. The solution was prepared as a weight standard (about 180 mg/g, 300 mg/ml) in 12*M* nitric acid, and the concentration was corrected for weight changes (due principally to radiolysis) on storage.

Plutonium–uranium standards. These were prepared by mixing the standard uranium and plutonium solutions in the required quantities. They were stored as weight standards (about 120 mg/g, 150 mg/ml) in 2*M* nitric acid solution and weight-change corrections were applied to these solutions.

Potassium dichromate standard solutions. Two solutions were prepared from P.V.S. grade potassium dichromate (Hopkin and Williams Ltd.) They were adjusted so that for the first, 1 g of solution was equivalent to 20·00 mg of uranium (about 0·17*N*, solution A) and for the second, 1 g was equivalent to 10·00 mg of plutonium (about 0·04*N*, solution B).

Titanium(III) sulphate solution. Titanium sponge (5 g) was warmed with a mixture of concentrated sulphuric acid (10 ml) and water (50 ml) until it had dissolved. The solution was stored in a 2-oz polythene bottle fitted with a dropper.

Sulphamic acid solution, 10% w/v.

Sample preparation

A weighed portion, about 0·5 g, of the mixed plutonium–uranium oxide sample was dissolved in 20 ml of 8*M* nitric acid/0·05*M* hydrofluoric acid mixture. The volume of solution was reduced to about 3 ml, then it was transferred to a tared flask, diluted to about 10 ml with 2*M* nitric acid and weighed. Weighed portions of the solution were taken for analysis.

Procedure

To provide a basis for development trials the procedure described by Corpel and Regnaud[8] was followed. The sample was transferred to the titration beaker and diluted to 40 ml with an acid mixture comprising 1*M* nitric–0·5*M* sulphuric–0·25*M* sulphamic acids. An excess of titanium(III) solution was added and the mixture was allowed to stand for 10 min to allow oxidation of surplus reductant to occur. The sample was then titrated with dichromate solution, potentiometry or amperometry being used to locate end-points for uranium and plutonium. In the preliminary study of the sequential oxidation, the dichromate solution was added from ordinary burettes; as titration conditions became established and data on precision and accuracy were needed, weight burettes were used. The weight burettes were used during the approach to the end-points, which were located precisely by further titration with dichromate delivered from the Agla Syringe.

RESULTS

Preliminary evaluation of end-point detection systems

Potentiometry. A brief study of the oxidation of uranium(IV) and plutonium(III) mixtures, using potentiometry with platinum and calomel electrodes and volumetric burettes, showed that only a single end-point was obtained. Variation in the acidity of the titration medium produced an ill-defined separation into two end-points at low acidity, but the titration was unsuitable for quantitative analysis. These results agree with other work.[8]

The titration of uranium(IV) and plutonium(III) separately, using constant-current potentiometry, gave good end-points for both species, and the titration curves were very different in character. It was found that a polarizing current of about 5 μA produced a well-defined titration curve for plutonium while one of 15 μA was needed for the uranium titration. Figure 2 shows curves for the separate titrations of plutonium(III) and uranium(IV) in a 0·5*M* sulphuric–1*M* nitric acid mixture. When mixtures of uranium and plutonium were titrated, two separate end-points were obtained, with the general shape expected from a knowledge of the individual uranium and plutonium titrations, but the uranium curve was markedly shifted on the voltage scale. A low-acid titration medium improved the quality of the two end-points, and

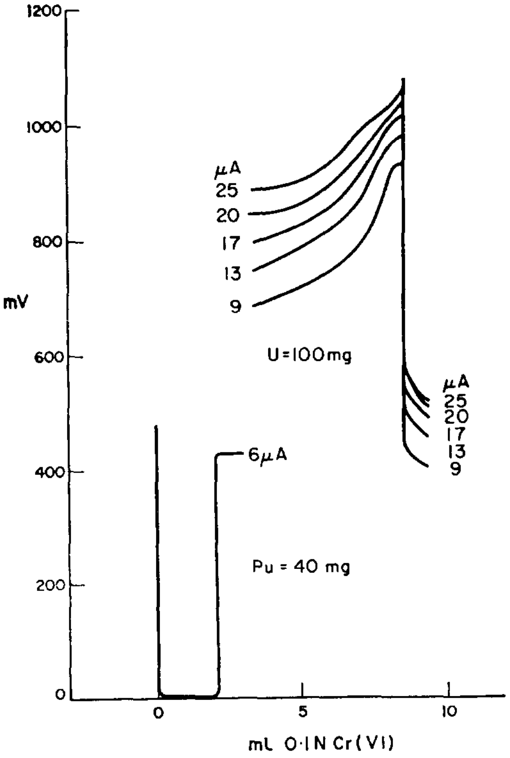


Fig. 2.—Constant-current potentiometry of separate uranium and plutonium samples in 1*M* HNO_3–0·5*M* H_2SO_4.

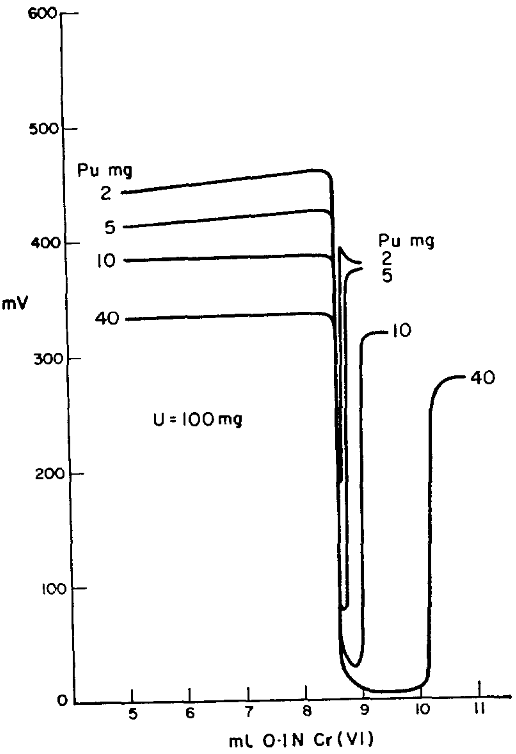


Fig. 3.—Constant-current potentiometry of uranium–plutonium mixtures in 0·2*M* HNO_3–0·2*M* H_2SO_4–0·2*M* NH_2SO_3H.

Fig. 3 shows the titration of uranium(IV) and varying amounts of plutonium(III) in $0{\cdot}2M$ sulphuric–$0{\cdot}2M$ nitric acids. A polarizing current of 15 μA was used. Although two separate end-points were obtained, the reproducibility of the determination of uranium and plutonium in mixtures was poor. A series of determinations on standards containing 15% plutonium showed a variation of several percent in the plutonium–uranium ratio results.

Amperometry. Solutions of uranium, plutonium and of mixtures of plutonium with uranium were titrated with dichromate solution, using a pair of electrodes polarized with a potential of about 200 mV. The titration of uranium(IV) produced no response in the indicator circuit at the titration equivalence point, as might be expected during the reaction of the two irreversible couples. The titration of plutonium(III) gave rise to an indicator current which increased to a maximum value, fell towards zero at the equivalence point and remained at a low constant value as further additions of dichromate were made. This behaviour is conventional for the titration of a reversible couple with an irreversible titrant, exemplified by plutonium(IV)–(III) and chromium(VI)–(III). When mixtures of uranium(IV) and plutonium(III) were titrated, a sharp rise in indicator current followed by a fall towards zero was observed for each addition of dichromate, at a stage well before the uranium equivalence point had been reached. The fall towards zero current was sluggish for titrations carried out in $0{\cdot}5M$ sulphuric–$1M$ nitric acids, but became more rapid when the acidity of the medium was lowered. Since it had been shown that an indicator current flowed only when both plutonium(IV) and plutonium(III) were present in the titration mixture, it was concluded that plutonium(IV) was formed during the titration before all of the uranium(IV) had been oxidized by the dichromate. The fall in current on standing presumably resulted from disappearance of the plutonium(IV) by interaction with uranium(IV), so that plutonium(IV) behaved as an important intermediate during the oxidation of uranium(IV) to (VI). It followed that the success of the sequential determination of uranium and plutonium would depend upon establishing conditions where the uranium(IV)–plutonium(IV) reaction was rapid and quantitative, to ensure precise location of the uranium end-point. The kinetics of this reaction have been studied,[12,13] and the most important feature of the reaction rate for the present application is its inverse dependence upon the square of the hydrogen ion concentration. The importance of the acidity of the titration medium in controlling the definition of the uranium end-point was thus established by the amperometric indicator system. After the uranium end-point had been passed and plutonium(IV) persisted during the titration with dichromate, stable indicator currents were produced and these current readings were used to locate the uranium end-point. After all the uranium had been oxidized, the plutonium(IV) concentration progressively increased and hence the current increased. The uranium end-point was given by the point of intersection of the (extrapolated) horizontal and rising lines of the titration curve.

The role of plutonium(IV) was demonstrated by using a standard solution of plutonium(IV) as titrant for a mixture of uranium(IV) and plutonium(III). Figure 4 shows the uranium end-point, which was within about 1% of that expected. After the uranium end-point had been passed, the total plutonium(III), *i.e.*, that present in the sample plus that formed by reaction of uranium(IV) with plutonium(IV), was

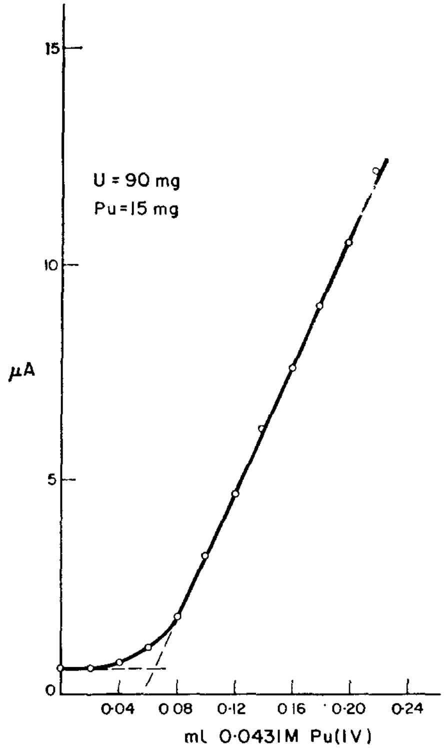


FIG. 4.—Amperometric titration of uranium(IV) with plutonium(IV).

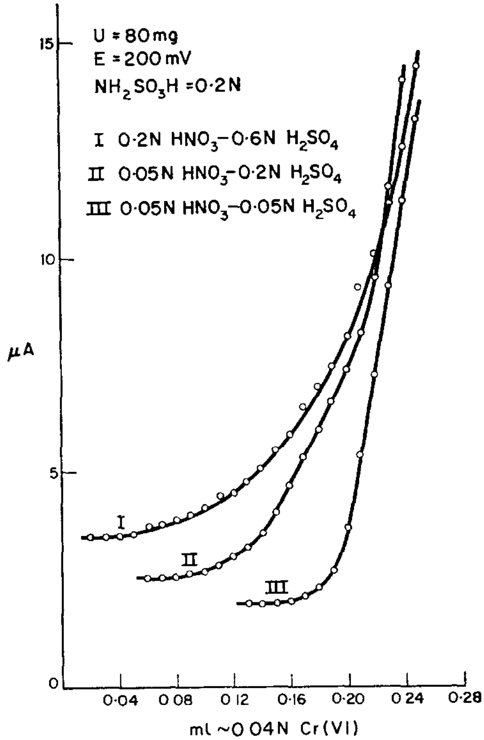


FIG. 5.—Effect of [H+] on the uranium end-point.

titrated with dichromate. The plutonium–uranium ratio result which was calculated for the sample was again within about 1% of that expected.

In view of the suitable response of amperometry to the plutonium(IV)–(III) couple, this technique was studied further.

Examination of amperometric titration variables

Effect of acidity. The effect of acidity on the uranium titration suggested that as low an acidity as possible would be an advantage. The acidity of the medium was found to be important for two other reasons.

(*a*) The reduction of the sample to the uranium(IV) and plutonium(III) oxidation states by titanium(III) requires a solution which is about 1*N* in both sulphuric and nitric acids.[8] The sulphuric acid controls the rate of oxidation of the excess of titanium(III) by nitric acid to ensure that quantitative reduction of the uranium and plutonium occurs. It was found that the chemical reduction could not be performed satisfactorily in a low-acid medium, and that it was necessary to reduce the sample in a small volume of 0·5*M* sulphuric–1*M* nitric acid, and then dilute the mixture to lower the acidity before titration.

(*b*) The extent to which the acidity of the medium could be lowered was limited by the quality of the plutonium end-point. Experiments in which the titration medium was less than 0·1*N* in both nitric and sulphamic acids and free from sulphuric acid showed that the plutonium end-point became impossible to locate, presumably because of disproportionation of the plutonium(IV). The addition of a small amount of sulphuric acid gave a much improved plutonium end-point. A medium comprising 0·05*M* nitric–0·025*M* sulphuric–0·2*M* sulphamic acids was found to be satisfactory for both uranium and plutonium end-point definition, and variation in the range 0·2–0·4*N* total acidity had little effect. The effect of acidity on the uranium titration curve is shown in Fig. 5, and typical uranium and plutonium titration curves are shown in Fig. 6. Under these conditions stable indicator currents were obtained 1–2 min after a dichromate addition had been made in the vicinity of the uranium end-point, but after this had been passed and plutonium(IV) persisted in the solution, current readings were stable within 30 sec.

Effect of applied voltage. During the development trials an arbitrarily chosen 200 mV had been applied across the electrodes. This value was confirmed as being most suitable by following titrations with different applied potentials. Figure 7 shows the effect of applied potential on the uranium end-point during the titration of mixtures having a plutonium–uranium ratio of about 15%. The plutonium end-point was also well-defined under these conditions.

Titration of plutonium and uranium standards. The titration of plutonium standards alone gave results showing a precision (3σ) of ±0·4% with 40–50 mg of plutonium. It

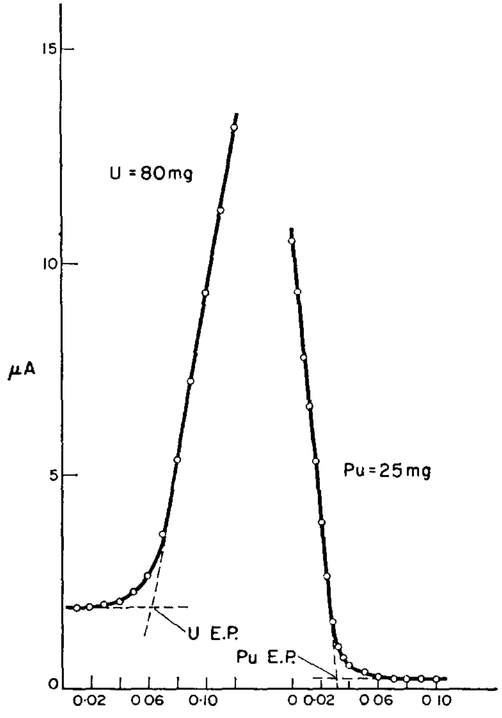


FIG. 6.—Typical end-points for uranium and plutonium.

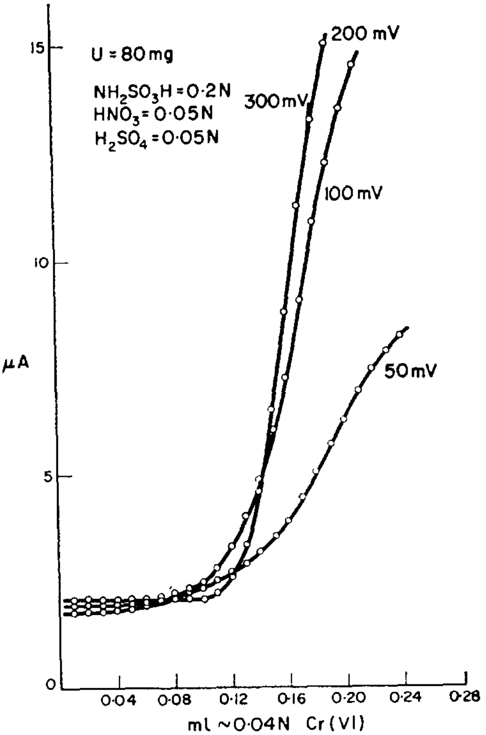


FIG. 7.—Effect of applied voltage on the shape of the uranium titration curve.

was not possible to obtain comparative data on uranium standards because of the inability of the amperometric end-point method to respond in the absence of an electrode depolarizer. Accordingly a plutonium–uranium standard containing about 15% plutonium was used to assess precision and accuracy. When the titration was carried out after the reduced sample had been diluted to lower the total acidity of the medium it was found that the uranium results obtained were lower than those expected for the standard by about 1%. Experiments in which the solutions were purged with inert gas to remove air gave results which were also low, and it was thought that atmospheric oxidation of the uranium(IV) was not the cause of the negative bias. A more likely explanation, although it was not proved, was that some disproportionation of the uranium(IV) occurred in the dilute acid. Whatever the cause of the bias, it was possible to minimize it by titrating part of the uranium(IV) with dichromate before the solution was diluted. Bias-free results were obtained when sufficient dichromate was added to oxidize about 90% of the uranium, the titration then being completed after dilution. To oxidize about 90% of the uranium presupposes knowledge of the uranium content of the sample. In the present application this did not create any special difficulties because plutonium–uranium mixed oxides are normally close to the specified plutonium–uranium ratio.

The procedure for the determination of uranium and plutonium would thus involve the sequence: reduction of the sample in 0·5M sulphuric–1M nitric acids, partial oxidation of the uranium(IV) with dichromate, dilution to reduce acidity, completion of the uranium titration, then titration of the plutonium. The full procedure is as follows

Recommended procedure for the determination of plutonium and uranium

If only the plutonium–uranium ratio of the sample is required then the oxide weight, solution weight and aliquot weight need not be measured accurately, but the same size of sample should be taken.

Weigh accurately into a 10-ml beaker an aliquot containing 100–150 mg of plutonium plus uranium. Add concentrated sulphuric acid (3 drops), evaporate just to fumes and dissolve the residue in warm 1M nitric acid (2 ml). Allow to cool, add 1M sulphamic acid (2 ml), followed by titanium(III) sulphate solution dropwise until the solution darkens in colour. This is usually accompanied by the evolution of nitrogen. Allow to stand for 10 min, during which time weigh the weight burette containing dichromate solution A to ±0·1 mg. Add sufficient of this solution to oxidize about 90% of the uranium estimated to be present, then transfer the sample solution to a 100-ml beaker with a solution of 1M sulphamic acid (8 ml) and water (30 ml). Start the stirrer, insert the electrodes and apply a potential of 200 mV across them. Stir for 5 min, after which time the initial high current will have fallen to a low value approaching zero. Continue dropwise addition of solution A until the indicator current shows a sharp rise followed by a slow fall to the original value; reweigh the weight burette.

Fill the Agla syringe with dichromate solution B and adjust the reading to zero. Mount it so that the tip just dips into the solution in the beaker. Add 0·01-ml increments and record the galvanometer and Agla readings after each addition. Allow 2 min between additions until the uranium end-point is passed, when the current begins to rise and stabilizes within 30 sec. Plot a graph of galvanometer deflection *vs.* volume added from the Agla and estimate the reading corresponding to the equivalence point, which is taken as the intersection of the horizontal and rising portions of the graph. Leave the Agla syringe in position with the tip immersed in the solution, fill a second weight burette with dichromate solution B and weigh to ±0·1 mg. Add this solution dropwise, when the current rises to a maximum and then begins to fall sharply. When the galvanometer deflection has fallen to 100–120 record the reading and reweigh the burette. Continue the titration with the Agla syringe, recording the Agla and galvanometer readings after each addition until the current falls to a constant value close to zero. Allow 30 sec between additions. Plot a graph of galvanometer deflection *vs.* volume added from the Agla and note the reading corresponding to the equivalence point. Calculate the weights of uranium and plutonium in the sample as follows:—

$$U = (20\,W_A + A_1 \times 4{\cdot}98)\ \text{mg}$$
$$Pu = 10[W_B + (A_2 - A_1)] - x\ \text{mg}$$

where W_A = weight of dichromate solution A

W_B = weight of dichromate solution B

A_1 = Agla reading (ml) at uranium equivalence point

A_2 = Agla reading (ml) at plutonium equivalence point

x = mg of Pu equivalent to the iron content of the titanium used

The uranium and plutonium content of the solid sample is obtained by multiplying each result by

$$\frac{\text{weight of sample solution in 10 ml flask}}{\text{weight of oxide specimen taken} \times \text{weight of solution analysed}}$$

These calculations are made on the assumption that 1 g of solution A is equivalent to 20·00 mg of uranium and that 1 g of solution B is equivalent to 4·98 mg of uranium and 10·00 mg of plutonium In practice, the appropriate factor must be used.

Performance of the method

Results on plutonium–uranium mixtures. Plutonium–uranium standards were analysed by the recommended procedure and the results obtained are shown in Table I.

The experimental results are calculated on the basis of dichromate as a primary standard. The agreement with the theoretical results shows that the method is free from bias at the plutonium–uranium ratios for which the method was designed, namely greater than about 15% plutonium. No results were obtained on mixtures intermediate between the 15% and 7% standards, hence the plutonium–uranium ratio at which the bias becomes significant is not known. The bias on the 7% mixture is most likely due to a combination of the plutonium–uranium ratio of the sample and the low concentration of plutonium present during the titration. It is possible that the use of a larger sample size would improve the results obtained at low plutonium–uranium ratios, but in a number of experiments where this was tried, difficulty was found in keeping the total acidity below the limit recommended. It was concluded that the optimum sample size under the conditions used was about 100 mg of plutonium plus uranium.

Two samples which were prepared from plutonium–uranium mixed oxides were analysed and the results compared with those from other methods in use in the Department. These results are shown in Table II.

The agreement between these results is good, particularly in view of the different physical bases of the methods.

Effect of impurities. From a knowledge of the plutonium assay method based on reduction by titanium(III)[8] it was expected that interference would be caused by iron, molybdenum, vanadium, arsenic and antimony. The most serious interference in the present method would thus be from iron, since this is likely to be the major impurity in plutonium–uranium oxides. Trials showed that iron interfered quantitatively with the plutonium but not with the uranium result. The effect of other elements is shown in Table III. High proportions of added element were employed to obtain an easily measurable effect. They were added at the sulphuric acid fuming stage of the method.

Molybdenum in the quantity added made the uranium end-point impossible to locate, and the total quantity of dichromate added to the plutonium end-point was

TABLE I.—ANALYSIS OF PLUTONIUM–URANIUM STANDARDS

Sample, *mg*	Theoretical			Experimental (mean)			Number of determinations	Precision (3σ)
	Plutonium, *mg/g*	Uranium, *mg/g*	Pu/(Pu + U)	Plutonium, *mg/g*	Uranium, *mg/g*	Pu/(Pu + U)		Pu/(Pu + U) %
105–110	8·16	114·5	0·0665	7·48	114·6	0·0612	18	3·8
100–105	17·67	101·0	0·1489	17·68	101·1	0·1488	23	0·54
50–55	14·63	83·0	0·1499	14·64	82·9	0·1501	18	1·44
85–90	24·02	71·8	0·2507	23·97	71·7	0·2505	20	0·70
100–105	29·70	88·4	0·2516	29·71	88·4	0·2516	23	0·58

TABLE II.—COMPARISON OF PLUTONIUM–URANIUM RATIO RESULTS

Sample	Sequential redox titration	Coulometry	X-Ray spectrometry
1	0·2394, 0·2393	0·2391, 0·2396	0·2395, 0·2397
2	0·2347, 0·2352	0·2347, 0·2350	0·2355, 0·2358

equivalent to the oxidation of the uranium and plutonium plus a one-electron oxidation of molybdenum.

Titration blank. It was found difficult to determine a true titration blank for the whole method. This was largely associated with the destruction of titanium(III) by the small amount of sulphuric–nitric acids used in the method when the amount of titanium(III) added in the blank was the same as that used for a plutonium–uranium sample. It was found however that titanium made a much greater contribution to the blank than any of the other reagents, and this contribution arose from iron as an impurity. Results from the chemical analysis of the titanium solution showed that the quantity of titanium(III) normally added during a determination would contain 32 μg of iron. The plutonium results quoted in Table I have been corrected for this quantity of iron. It was found necessary to determine iron in each batch of titanium(III) sulphate solution prepared.

TABLE III.—EFFECT OF IMPURITIES

Element	Amount, *mg*	Effect
Manganese	5	None
Tin	10	None
Tungsten	25	Precipitate, which dissolved on dilution. No interference
Copper	5	Precipitate, which dissolved on dilution. Low uranium result
Molybdenum	10	Masked uranium end-point
Vanadium	10	Quantitative interference with plutonium
Simulated mixed fission products	*	None

* The amount of inactive simulated mixed fission product added was equivalent to the quantities expected to be associated with 100 mg of plutonium plus uranium irradiated to 5 % burn-up and cooled for 6 months.

Behaviour of the indicator electrodes. Recommended procedures vary widely for the pretreatment of electrodes in polarized indicator circuits to ensure reproducibility and sensitivity. Some authors recommend electrolytic treatments (*e.g.*, ref. 10) while others prefer chemical procedures (*e.g.*, ref. 14). The choice of the most suitable pretreatment method appears to be largely associated with the particular system being studied, and a procedure which is suitable for electrodes which are exposed to strongly reducing conditions during a titration may not be suitable for those which experience strongly oxidizing conditions. In the present application the electrodes were treated initially by cleaning with hot chromic acid. Before use they were immersed for 5 min in a solution of 0·25*M* sulphamic acid containing a few drops of saturated iron(II) ammonium sulphate solution. After each titration they were again immersed in this iron(II) solution then rinsed with water before the next titration. The electrodes were stored overnight in sample solution which had been titrated beyond the plutonium end-point. When their performance began to deteriorate the procedure was repeated. The behaviour of the electrodes during a series of 20 runs is illustrated by the uranium titration end-points shown in Fig. 8. The results of the first two runs were normally discarded.

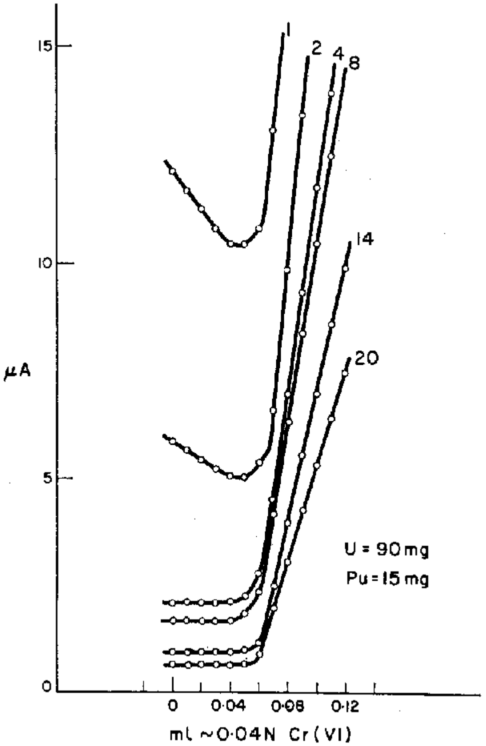


FIG. 8.—Performance of the electrodes in a series of titrations after thorough cleaning.

DISCUSSION

The method, which was developed for the sequential determination of plutonium and uranium, was found to be rapid and convenient to perform. Starting at the solution stage it may be completed within about 1 hr, which represents an appreciable saving in analysis time compared with separate redox titration methods for plutonium and for uranium in mixed oxides. The sequential procedure has the added advantage that when only a plutonium–uranium ratio result is required on the mixed oxide, the complete assay procedure is not needed. The precise weighing of the solid sample and quantitative preparation of solution may be eliminated, and the sampling arranged so that the portion of solution taken for analysis contains 100–120 mg of plutonium plus uranium.

An important feature of the sequential method, namely its reliance on the reaction between plutonium(IV) and uranium(IV), is common to the controlled potential coulometric method developed in this Department.[15] A difference between the two methods however is the smaller dependence upon acidity of the reaction medium in the coulometric method. This is related to other factors influencing the rate of the uranium(IV)–plutonium(IV) reaction in coulometry, primarily the concentration of plutonium(IV). In the coulometric method plutonium(IV) is continuously generated at the working electrode so that the final products of electrolysis are uranium(VI) and plutonium(IV). At no time do the concentrations of both uranium(IV) and plutonium(IV) tend towards zero, as they do during the redox titration method. Presumably at the uranium equivalence point in the redox method the rate of reaction between uranium(IV) and plutonium(IV) becomes very small as the concentrations of these species attain the low values defined by the equilibrium constant. The degree of rounding of the amperometric end-point for uranium is typical of many other redox systems. A better redox-titration analogy of the coulometric method would be the oxidation titration of uranium(IV) and plutonium(III) to uranium(VI) and plutonium(IV) followed by the reduction titration of plutonium(IV) to (III).

The amperometric indicator circuit was found to be useful in gaining information on the oxidation of uranium and plutonium mixtures and it provided sensitive and reproducible indication of the end-points. The constant-current potentiometric procedure was examined only briefly but it would be unlikely to be as satisfactory as amperometry. The electrode reactions giving rise to the observed potential changes were clearly complex, and the modification to the uranium titration curves caused by plutonium suggests that the latter was being oxidized or reduced at the electrodes. It is conceivable that in a complex system of reversible and irreversible couples, biased results may be obtained. In the worst case, for example, where the oxidation of plutonium(III) at one electrode is not accompanied by an equivalent reduction of plutonium(IV) at the other, the electrolysis resulting from the passage of a 20 μA current during a titration lasting 40 min would cause a bias of about 0·7% on 15-mg quantities of plutonium.

Zusammenfassung—Die Benutzung einer Folgebestimmung von Uranium und Plutonium in einer einzigen Musterlösung bringt Ersparnis in der Analysezeit und Apparatebeanspruchung. Das Verfahren beginnt mit U(IV) und Pu(III) in einer Mischung von Schwefel- und Stickstoffsalzen. Titrierung mit Bichromat mit Ampèremessung an einem Paar polarisierbarer Elektroden ergiebt entsprechend der Folgeoxydierung von U(IV) auf U(VI) und Pu(III) auf Pu(IV) zwei gut erkennbare Endpunkte. Die mengenmässige Oxydierung von U(IV) auf U(VI) wird über die Wirkung von Pu(IV) als Zwischenprodukt erreicht und hängt von der Gründung von Bedingungen ab, welche schnelle Reaktion zwischen U(IV) und Pu(IV) begünstigen. Das Verfahren ist präzise und genau. Bei Pu-U Mischungen mit einem Gehalt zwischen 15 und 30% Plutonium ist die Präzision (3σ) der Verhältnisergebnisse Pu:U ± 0,6% für Muster mit 100–120 mg Plutonium plus Uranium. Eisen und Vanadium wirken mengenmässig störend auf Plutonium ein, Kupfer wirkt, nicht mengenmässig, störend auf Uranium ein, und grosse Mengen von Molybdän verhüllen den Uranium Endpunkt.

Résumé—L'emploi d'un dosage séquentiel de l'uranium et du plutonium dans une seule solution d'échantillon a pour résultat une économie dans le temps d'analyse et les exigences instrumentales. La méthode part de U(IV) et Pu(III) dans un mélange d'acides sulfurique et nitrique. Le titrage au bichromate, utilisant l'ampérométrie sur une paire d'électrodes polarisables, produit deux points de fin de dosage bien définis correspondant à l'oxydation séquentielle de U(IV) en U(VI) et de Pu(III) en Pu(IV). L'oxydation quantitative de U(IV) en U(VI) est réalisée *via* l'action de Pu(IV) comme intermédiaire, et dépend de l'établissement de conditions qui favorisent la réaction rapide entre U(IV) et Pu(IV). La méthode est juste et précise. Avec des mélanges Pu–U contenant entre 15 et 30% de plutonium, la précision (3σ) des résultats des rapports Pu:U est de ±0,6% pour les échantillons contenant 100–120 mg de plutonium plus uranium. Le fer et le vanadium interfèrent quantitativement avec le plutonium, le cuivre interfère de manière non-quantitative avec l'uranium, et de grandes quantités de molybdène masquent le point de fin de dosage de l'uranium.

REFERENCES

1. J. L. Drummond and R. A. Grant, *Talanta*, 1966, **13,** 477.
2. W. Davies and W. Gray, *ibid.*, 1964, **11,** 1203.
3. J. Cherry, J. Holmes and J. J. B. Williams, *U.K. At. Energy Authority Prod. Group*, *P.G. Rep.* 832(W), 1968.
4. J. Cherry, *ibid.*, 827(W), 1968.
5. G. B. Nelson, K. A. Bergstresser, G. R. Waterbury and C. F. Metz, *12th Conf Anal. Chem. Nuclear Technol.*, 1968 Gatlinburg, Tenn., Paper 13.
6. A. von Baeckmann and L. Lindner, *Angew. Chem. Intern. Ed.*, 1967, **6,** 268.
7. H. Kramer, *U.S. At. Energy Comm. Rep.* NBL-159, 1960, p. 28.
8. J. Corpel and F. Regnaud, *Anal. Chim. Acta*, 1962, **27,** 36.
9. F. Hazel and W. McNabb, *Anal. Chem.*, 1950, **22,** 654.
10. T. M. Florence and P. J. Shirvington, *ibid.*, 1965, **37,** 950.
11. R. H. Betts, *Can. J. Chem.*, 1955, **33,** 1780.
12. T. W. Newton, *J. Phys. Chem.*, 1959, **63,** 1493.
13. P. Biddle, J. H. Miles and M. J. Waterman, *J. Inorg. Nucl. Chem.*, 1966, **28,** 1736.
14. G. Marinenko and J. K. Taylor, *J. Res. Natl. Bur. Std.*, 1963, **67A,** 453.
15. J. B. Fardon and I. R. McGowan, *Talanta*, 1972, **19,** 11.

Talanta, 1972, Vol. 19, pp. 1349 to 1354. Pergamon Press. Printed in Northern Ireland

FLUORIDE DETERMINATION WITH A MICRO FLOW-CALORIMETER

CARL E. JOHANSSON
Department of Analytical Chemistry, Chemical Center, University of Lund,
Lund, Sweden*

(*Received* 15 *February* 1972. *Accepted* 18 *March* 1972)

Summary—Fluoride is determined by an integration technique with a flow calorimeter. All samples are absorbed on an anion-exchange resin before being brought into the calorimetric system. The reaction between hydrofluoric acid and sodium hydroxide is used in the determinations. The method is applied to samples with between 7 μg and 5 mg of fluoride. The confidence limit is $\pm 2{\cdot}5\ \mu g$ for small samples and $\pm 25\ \mu g$ for large samples. The enthalpy of the reaction $H^+ + F^- \rightarrow HF_{(aq)}$ was found to be $13{\cdot}77 \pm 0{\cdot}08$ kJ/mole.

THE ENTHALPIMETRIC determination of fluoride has been described in a previous article.[1] Samples of 6–8 mg of sodium fluoride could be determined with an injection technique and 40–400 μg with a flow calorimetric technique. With the method presented here the amounts are not so restricted and the range is 15 μg–10 mg of sodium fluoride.

In an enthalpimetric titration with a flow calorimeter of the heat leakage type, two calorimetric liquids are brought together in a mixing cell where heat effect is produced. If the temperatures of the solutions before the reaction are equal and constant, and the flow rate is kept constant, the heat effect is also constant during the experiment. The electrical output from the thermocouples is proportional to the heat effect,[2] which is caused by various factors including friction, dilution and reaction. When one of the solutions is in stoichiometric excess, the heat of reaction between them is proportional to the concentration of the other solution.

Zero adjustment of the output is done with a blank solution. When this is exchanged with a sample solution, the temperature in the cell rises until a steady state is reached.[3] This means that the heat leakage from the cell is equal to the heat entering the cell. When the sample is delivered into the blank solution as a normally distributed concentration gradient, the output signal will not refer to a steady state. However, the output signal will often closely resemble the real concentration curve. The integral of the output signal is then proportional to the amount of the sample. If the molar heat of reaction depends on the concentration, the integrated voltage *vs.* sample curve can still approximate to a straight line for narrow concentration ranges.

A problem in enthalpimetric measurements is to achieve good selectivity. With the usual technique a contaminant can give an error in the signal without being discovered. However, if the sample is separated from disturbing contaminants by a chromatographic process, it is possible to measure the amount of substance by integrating the output voltage. The slope of the signal on the recorder will indicate if there are any contaminants in the reacting substance.

As fluoride ions are easily separated from many other anions by anion-exchange, they may be determined conveniently by the integration technique. When the eluent is hydroxide solution, the alkaline fluoride solution is best converted into a dilute

---

* Present address: Statens Livsmedelsverk, Stockholm 60, Sweden.

hydrofluoric acid solution with a cation-exchange resin in H$^+$-form. The reaction measured in the flow cell is then a simple acid–base reaction.

When thermodynamic properties are to be measured, the integration technique is not very suitable since the values depend on the sample concentration. The ΔH of dissociation of hydrofluoric acid was therefore measured by the usual steady-state technique.

EXPERIMENTAL

Quantitative determination of fluoride

Reagents. The sample solutions were prepared from sodium fluoride of Suprapur quality (Merck), and sodium carbonate, chloride, phosphate, sulphate and sulphide all of *pro analysi* quality. In the oxygen-flask combustion samples of 2–5 mg of *p*-fluorobenzoic acid of *pro analysi* quality were used. The eluent in the anion-exchange was sodium hydroxide solution prepared from a concentrated, carbon dioxide-free solution. The anion-exchange resins were regenerated with $4M$ sodium hydroxide and the cation-exchange resins with $3M$ hydrochloric acid. The reagent solution in the enthalpimetric measurements was $0{\cdot}1M$ sodium hydroxide.

Oxygen combustion. The *p*-fluorobenzoic acid samples were wrapped in a paper sample carrier. Two drops of dodecyl alcohol and 2 mg of potassium chlorate were added as combustion aid and the carrier was enclosed in a platinum basket attached to a platinum wire on a rubber stopper. The paper was ignited and put into a 500-ml Nalgene polycarbonate flask[4] which had been flushed with oxygen. The flask also contained 5 ml of $0{\cdot}05M$ sodium hydroxide. The resulting sodium fluoride solution was adjusted to pH 5·2 with $0{\cdot}003M$ nitric acid and purged with carbon dioxide-free nitrogen for 15 min. The solution was then handled according to ion-exchange procedure II.

Ion-exchange procedure I. Fluoride was separated from other anions by anion exchange in a similar manner to that previously described.[1] Samples containing 1·000 mg of sodium fluoride and an 80-fold excess of carbonate, chloride, phosphate, sulphate and sulphide were put on a glass column with 2·5 g of Dowex 1 × 8, 200–400 mesh in OH-form. The flow-rate in the absorption step was 1 ml/min. After a wash with distilled water, the fluoride was eluted with $0{\cdot}2M$ sodium hydroxide at 1 ml/min. The first 20 ml of effluent did not contain any fluoride and were rejected. The following 50 ml contained all the fluoride and were passed through a Teflon column with 5 g (dry weight) of Dowex 50 W × 8, 20–50 mesh in H$^+$-form, and after that through 1 g of the resin in Na$^+$-form. The resulting sodium fluoride solution was adjusted to a pH of 5·2 with $0{\cdot}003M$ nitric acid and purged with carbon dioxide-free nitrogen for 15 min. Samples containing carbonate were also adjusted to pH 5·2 and purged with nitrogen before the ion-exchange procedure. The ion-exchange resins were regenerated and washed with distilled water before the next sample was introduced.

When the amounts of other anions are in the range <0·05 mmole, procedure I is not necessary and the determination can be done directly through procedure II. If any of the contaminants does pass through during the integration time it is easily detected on the recorder signal.

Procedure I was not used in direct connecton with the calorimetric step for the following reasons: (*a*) the flow-rate of the eluent, which was controlled by the pressure from a nitrogen cylinder, could not be reproduced with good precision, (*b*) the fluoride concentration peak was too broad, (c) the concentration of carbonate ions was relatively high in spite of the precautions taken.

Ion-exchange procedure II. The fluoride–nitrate solution from procedure I was absorbed on 0·5 g of an anion-exchange resin, Dowex 1 × 8, 200–400 mesh in OH$^-$-form. The resin was then connected with a 5-mm diameter PVC tube filled with 3 g of Dowex 50 W × 8 resin, 20–50 mesh in H$^+$-form. Sodium hydroxide ($0{\cdot}1M$) was pumped through the anion-exchange resin to elute the fluoride. The nitrate ions remained in the resin. The solution passed through the cation-exchange resin and the sodium ions were exchanged for hydrogen ions. The resulting hydrofluoric acid passed on to the calorimeter. Calibration samples with 15 μg–10 mg of sodium fluoride were also treated as in procedure II.

The anion-exchange resins were regenerated with $4M$ sodium hydroxide and washed with distilled water. The cation-exchange resins were regenerated with $3M$ hydrochloric acid and washed with distilled water after every third sample.

Calorimeter. A commercial instrument, the LKB 10700-1 was used[2] (Fig. 1). This calorimeter is a twin heat-leakage calorimeter utilizing semiconducting thermocouple plates for measurements of the heat flow. The mixing cell was made of a gold spiral and had an internal volume of 0·6 ml. An LKB 10200 and an LKB 12000 Perspex Pump were used to pump the reagent and the sample solutions through the reaction cell. The signal from the thermocouples was fed to a Keithley 150 B Amplifier with the input signal measured in the 3-mV range.

The time-voltage curve was followed on a Servogor RE 511-recorder. The integration unit consisted of an electronic integrator. The integrated signal was measured on a Dynamco DM 2006 Digital Voltmeter in the ranges 100 mV, 1 V and 10 V, depending on the amount of fluoride in the sample.

Calorimetric procedure. The reagent solution of 0·1*M* sodium hydroxide in the calorimetric step was pumped into the calorimeter at a rate of 32·2 ml/hr. The blank solution was 0·1*M* sodium hydroxide. It was first passed through an anion-exchange resin in the OH^--form which absorbed the carbonate ions and then through a cation-exchange resin in the H^+-form at a rate of 33·5 ml/hr. When a steady state was reached, the output signal from the amplifier was adjusted to zero. Then the anion-exchange resin was exchanged with the sample resin and procedure II was followed. About 15 min after the anion-exchange resin with the sample was connected, the hydrofluoric acid reached the calorimetric cell and reacted with the sodium hydroxide solution. The output signal increased and reached a maximum about 5 min later, and after 20 min the signal had returned to the zero level. The temperature in the calorimeter was 25°.

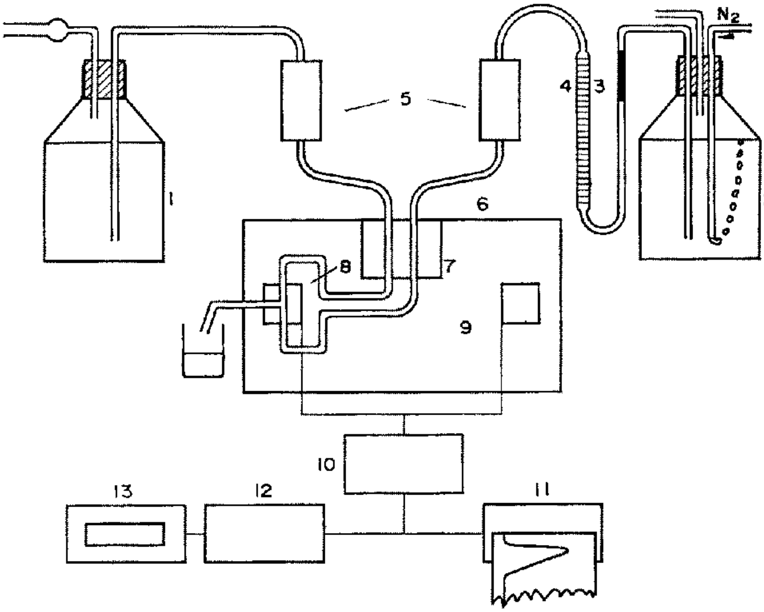


FIG. 1.—Equipment for the fluoride determination.

1,2. Bottles with 0·1*M* sodium hydroxide.
3. Ion-exchange resin Dowex 1 × 8 with fluoride sample.
4. Ion-exchange resin Dowex 50W × 8.
5. Peristaltic pumps.
6. Calorimeter.
7. Temperature adjustment.
8. Calorimetric cell.
9. Reference cell.
10. Amplifier.
11. Recorder.
12. Integrator.
13. Voltmeter.

Determination of the enthalpy change for the acid-base reaction

The enthalpy change of the reaction between sodium fluoride and 0·2*M* hydrochloric acid was measured for different concentrations of the salt. As a comparison, the enthalpy change of the reaction between hydrochloric acid and sodium hydroxide was also measured.

Reagents. Hydrochloric acid solutions with concentrations between 0·005 and 0·01*M* were made from concentrated acid, and the reagent solution 0·1*M* sodium hydroxide made from a concentrated carbon dioxide-free solution.

Calorimeter. The same equipment was used as in the quantitative determinations. The heater in the reaction cell had a resistance of 49·816 Ω. The Keithley 150 B Amplifier was used on the 300-μV range and the output measured with the Dynamco DM 2006 Digital Voltmeter on the 100-mV range. The temperature of the calorimeter was 25°.

Calorimetric procedure. An electrical calibration was performed with the heater in the reaction cell. The liquids were $0{\cdot}1M$ sodium hydroxide and distilled water. The output voltage was measured for calibration currents between 3 and 10 mA. The flow-rates were the same as in the quantitative measurements, 33·5 ml/hr for the distilled water and 32·2 ml/hr for the sodium hydroxide. The distilled water was then replaced with hydrochloric acid. The output voltage was measured for different acid concentrations. The hydroxide was then exchanged for distilled water and the heat of dilution was measured for different concentrations of the acid solutions. Then the output voltage was measured for different concentrations of fluoride reacting with $0{\cdot}2M$ hydrochloric acid.

RESULTS AND DISCUSSION

The reaction between hydrogen fluoride and hydroxide consists of two steps: the dissociation of hydrogen fluoride and the reaction between hydrogen ions and hydroxide ions. The dissociation of hydrogen fluoride decreases with increasing concentration. Because the heat of dissociation, as shown later, is relatively high, the molar heat of reaction between hydrofluoric acid and hydroxide increases with increasing concentration of the acid. It is obvious that the voltage-time curve on the recorder must be the same for different determinations of the same amount of fluoride if reproducible results are to be obtained. This was achieved in the procedure described. Since the molar heat of reaction is different for different concentrations of fluoride, the plot of integrated voltage *vs.* amount of sample is not a straight line, but over short intervals, approximates to one, and the precision of the method in different concentration ranges could be calculated by regression analysis. For an unknown sample in duplicate the amount of fluorine could be determined within the ranges shown in Table I (95% confidence limits).

TABLE I.—PRECISION OF FLUORIDE DETERMINATION.

Fluoride taken, *mg*	Precision at a confidence limit of 95% *mg*	Number of determinations
0·007–0·02	±0·0025	7
0·02–0·3	±0·0065	7
0·3–2	±0·0065	13
2–5	±0·025	14

The best relative precision is given in the concentration range 0·3–2 mg of fluoride. For larger amounts the reproducibility is not so good. The reason could be that the samples are absorbed on a larger area of the ion-exchange resin and therefore give less reproducible time–concentration curves in the elution step. Since the molar heat of reaction is dependent on the concentration, the integrated voltage can then differ for the same amount of fluoride.

In Table II results from the oxygen-flask combustion experiment are shown. The value of the integrated signal from the calorimetric procedure is used to calculate the amount of the fluorine, from the calibration curve in the 0·3–2 mg range.

The source of the recorder signal is easily identified through a spot test.[5] It is also possible to absorb the fluoride on an anion-exchange resin after it has passed through the reaction cell and then let it go through the calorimetric procedure once more.

The microcalorimeter can possibly also be used as a detector in other chromatographic processes, *e.g.*, liquid partition chromatography.

TABLE II.—DETERMINATION OF FLUORINE IN *p*-FLUOROBENZOIC ACID.

F added, *mg*	F found from calibration curve *mg*	Error, *mg*
0·2719	0·2660	−0·0059
0·3064	0·3102	+0·0038
0·4927	0·4979	+0·0052
0·4996	0·4906	−0·0090
0·5499	0·5500	+0·0001
0·6007	0·5978	−0·0029
0·6110	0·6101	−0·0009

TABLE III.—DETERMINATION OF FLUORIDE IN THE PRESENCE OF OTHER ANIONS.

F added, *mg*	Other anions, 0·5*M*, 2 ml of each	F found, from calibration curve, *mg*	Error, *mg*
0·452	PO_4^{3-}, S^{2-}	0·455	+0·003
0·452	PO_4^{3-}, S^{2-}	0·450	−0·002
0·452	CO_3^{2-}, Cl^-	0·452	±0
0·452	SO_4^{2-}, Cl^-	0·455	+0·003

Enthalpy change determination

The output voltages for calibration currents used here (3–10 mA) were directly proportional to the heat energy RI^2. A straight calibration line was established for output voltage *vs.* energy.

The heats of the actual reactions could be calculated from the calibration line. In the hydrochloric acid–sodium hydroxide reaction, the enthalpies at concentrations of the acid between 0·005*M* and 0·01*M* and ionic strength 0·1*M* were measured. The values for infinite dilution were then calculated.[6,7] The enthalpy of the ionization of water at infinite dilution was 56·03 ± 0·26 *kJ*/mole. This is in fairly good agreement with values in the literature.[6,8]

Table IV shows the molar enthalpies measured at ionic strength 0·1*M* for the reaction between sodium fluoride (at different concentrations) and hydrochloric acid, including the heat of dilution of the fluoride solution. The concentration of HF_2^- formed is $<3 \times 10^{-4}$. [HF].[7] The heat of formation of HF_2^- was calculated

TABLE IV.—MOLAR ENTHALPIES FOR NaF + HCl REACTION AT DIFFERENT SALT CONCENTRATIONS.

[NaF], *M*	ΔH, *kJ/mole*	ΔH at infinite dilution, *kJ/mole*
0·0050	13·38	13·78
0·0050	13·40	13·80
0·0067	13·36	13·80
0·0067	13·49	13·93
0·0100	13·28	13·63
0·0100	13·26	13·67
0·0100	13·28	13·70
0·0233	13·26	13·85

from Hepler *et al.*[9] to be ~16 *kJ*/mole. The influence of this on the results was therefore neglected.

The enthalpy of the reaction $H^+ + F^- \rightarrow HF_{(aq)}$ at infinite dilution and 25° is then 13·77 ± 0·08 *kJ*/mole, which is rather different from the value given by Hepler *et al.*[9] of 13·31 ± 0·06 *kJ*/mole.

Acknowledgement—I wish to thank Dr. K. J. Karrman for valuable help during this work and Miss Birgitta Rees for performing the oxygen-flask combustions. I am also thankful to the Swedish National Research Council for defraying the cost of the calorimeter.

Zusammenfassung—Fluorid wird in einem Durchflußkalorimeter mit Hilfe eines Integrationsverfahrens bestimmt. Ebe die Proben ins Kalorimetersystem gebracht werden, werden sie an einem Anionenaustauschharz adsorbiert. Bei den Bestimmungen wird die Reaktion zwischen Flußsäure und Natriumhydroxid ausgenutzt. Das Verfahren wird auf Proben mit 7 μg bis 5 mg Fluorid angewandt. Die Vertrauensgrenze beträgt ± 2,5 μg bei kleinen und ±2,5 μg bei großen Proben. Für die Enthalpie der Reaktion $H^+ + F^- \rightarrow HF(aq)$ wurde der Wert 13,77 ± 0,08 kJ/Mol gefunden.

Résumé—On dose le fluorure par une technique d'intégration avec un calorimètre à écoulement. Tous les échantillons sont absorbés sur une résine échangeuse d'anions avant d'être introduits dans le système calorimétrique. On utilise la réaction entre l'acide fluorhydrique et la soude dans les dosages. La méthode est appliquée à des échantillons contenant entre 7 μg et 5 mg de fluorure. La limite de confiance est de ±2,5 μg pour les petits échantillons et ±25 μg poru les gros échantillons. On a trouvé que l'enthalpie de la réaction $H^+ + F^- \rightarrow HF$ (aq) est de 13,77 ± 0,08 kJ/mole.

REFERENCES

1. C. E. Johansson, *Talanta*, 1970, **17**, 739.
2. I. Wadsö and P. Monk, *Acta Chem. Scand.*, 1968, **22**, 1851.
3. P. T. Priestley, W. S. Sebborn and R. F. W. Selman, *Analyst*, 1965, **90**, 589.
4. T. S. Light and R. F. Mannion, *Anal. Chem.*, 1969, **41**, 107.
5. F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Ed., Elsevier, Amsterdam, 1966.
6. C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, 1963, **67**, 2608.
7. *Selected Values of Chemical Thermodynamic Properties*, *Natl. Bur. Std. Circ.*, No. 500, 1952.
8. J. D. Hale, R. M. Izatt and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2611.
9. L. G. Hepler, W. L. Jolly and W. M. Latimer, *J. Am. Chem. Soc.*, 1953, **75**, 2809.

Talanta, 1972, Vol. 19, pp. 1355 to 1362. Pergamon Press. Printed in Northern Ireland

SYNTHESIS AND ION-EXCHANGE PROPERTIES OF CERIC ANTIMONATE

SEPARATION OF Hg^{2+} FROM Zn^{2+}, Cd^{2+}, Pb^{2+} AND Tl^{+}; Cu^{2+} FROM Mn^{2+}; Fe^{3+} FROM Al^{3+}; AND Zr^{4+} FROM Th^{4+}

J. S. GILL and S. N. TANDON
Chemical Laboratories, University of Roorkee, Roorkee (U.P.) India

(*Received* 25 *February* 1972. *Accepted* 5 *April* 1972)

Summary—Ceric antimonate has been prepared under varying conditions of precipitation. Its properties and ion-exchange behaviour have been studied. Separations of Hg^{2+} from Zn^{2+}, Cd^{2+}, Pb^{2+} and Tl^{+}; Cu^{2+} from Mn^{2+}; Fe^{3+} from Al^{3+}; and Zr^{4+} from Th^{4+} have been achieved with this material.

IN THE LAST DECADE a good deal of interest has grown in synthetic inorganic ion-exchangers.[1] This is mainly because of their greater power to withstand higher radiation doses and temperatures than the commonly-used organic-based resins. In addition to this they sometimes exhibit highly specific properties which might permit improved separations under ordinary conditions. A large number of insoluble salts formed from multivalent metals and polybasic acids have been investigated as inorganic ion-exchangers. Although most of the work deals with studies on zirconium phosphate, other phosphates, arsenates, antimonates, tungstates, molybdates and hydrous oxides have also been studied as potential ion-exchangers. Amongst the antimonates of quadrivalent elements which form an equally promising series, zirconium[2,3] and tin(IV)[4] antimonates have already been investigated by earlier workers. In continuation of our systematic studies on some new inorganic ion-exchangers[5,6] ceric antimonate was explored for its ion-exchange properties.

The present report summarizes our findings on the preparation, properties and ion-exchange behaviour of ceric antimonate. The conventional method of precipitating ceric antimonate with potassium pyroantimonate gives a product unsuitable for column operation. But the samples prepared with antimonic acid can be conveniently used in columns. Not only this, they also exhibit higher exchange capacity. The distribution ratios for 21 different metal ions have revealed that the exchanger is more or less specific for Hg^{2+}, which has been separated from closely associated elements such as Zn^{2+}, Cd^{2+}, Pb^{2+} and from Tl^{+} which is of interest in nuclear reaction studies. Besides this, other separations of analytical importance such as Cu^{2+} from Mn^{2+}; Fe^{3+} from Al^{3+}; Zr^{4+} from Th^{4+} have also been achieved on this material.

EXPERIMENTAL

Reagents

Ceric ammonium sulphate and potassium pyroantimonate were used without further purification.

Amberlite IR-120 ion-exchange resin (H^{+} form) was used for preparing antimonic acid.

^{203}Hg, ^{65}Zn, ^{115m}Cd, ^{58}Co, ^{204}Tl, $^{55+59}Fe$ and ^{51}Cr radioisotopes were used for the determination of distribution ratios.

All other reagents used were of analytical grade.

Preparation of ceric antimonate

All the samples of ceric antimonate were prepared by methathesis of Ce^{4+} and $[Sb(OH)_6]^-$ ($K[Sb(OH)_6]$ or $H[Sb(OH)_6]$) at room temperature (14 ± 3°). Details of precipitation are summarized in Table I. The precipitate was allowed to settle at room temperature for 4 hr. It was filtered off, washed thoroughly with demineralized water and dried in air at room temperature. The samples obtained with potassium pyroantimonate were sieved to 100–200 mesh. The precipitation with antimonic acid yielded gels which were broken to smaller particles by immersion in water. In cases where the gel did not break down to the desired particle size it was ground in a porcelain mortar and sieved to 100–200 mesh size for batch operation and 50–100 mesh size for column operation. To convert the ion-exchanger into the hydrogen form, it was immersed in 1–2*M* mineral acid for 2–3 days with intermittent shaking and renewal of acid. It was then washed several times with demineralized water and dried in air.

TABLE I.—METHODS OF PREPARATION, COMPOSITION AND EXCHANGE CAPACITY OF THE CERIC ANTIMONATE PRODUCTS (dried at room temperature, 14 ± 3°C).

Sample no.	Initial pH of Ce^{4+}	Concentration of reagents in mixed solution		Volume of mixed solution, *ml*	Sb(V)/Ce(IV)	Hydrogen liberation capacity, *meq/g*	Hydrogen absorption capacity, *meq/g*
		Ce^{4+}, *M*	$[Sb(OH)_6]^-$, *M*				
1A	2·0	0·025	0·025	200	0·30	0·69	0·63
2A	1·5	0·025	0·025	200	0·30	0·71	0·69
3A	1·0	0·025	0·025	200	0·31	0·83	0·80
4A	0·75	0·025	0·025	200	0·32	0·88	0·82
5A*	0·75	0·025	0·025	200	0·32	1·22	1·12
6B*	0·75	0·025	0·025	200	0·33	1·23	1·18
7A*	0·75	0·025	0·050	200	0·32	1·20	1·09
8A*	0·75	0·050	0·025	200	0·31	1·17	1·08

* Samples prepared by precipitating with antimonic acid.
A—Antimonate solution added to ceric solution.
B—Ceric solution added to antimonate solution.

Composition of ceric antimonate

Known amounts of ceric antimonate samples were dissolved in hot concentrated hydrochloric acid. In one portion cerium was estimated[7] as Ce(III) spectrophotometrically at 254 nm and in another portion Sb(V) was determined gravimetrically[8] by precipitation as Sb_2S_5. Ce(IV) and Sb(V) ratios are reported in Table I. To test the accuracy of the method of determining cerium:antimony ratios, control experiments and blanks were run.

Properties

All samples were yellow in colour. The samples obtained from potassium pyroantimonate were powdery, those from antimonic acid were in the form of a gel and could be sieved to the desired mesh size. The thermogravimetric curve of a typical sample (5A) recorded at an average heating rate of 5°/min shows a continuous loss in weight up to about 400°.

The chemical stability of sample 5A in various solutions was examined with the following results.

(*a*) All mineral acids up to 4*M* have no effect in the cold, but on heating the ion-exchanger starts dissolving.

(*b*) Alkalis of all concentrations have no effect.

(*c*) The ion-exchanger was stable in water, alcohol, benzene, acetic acid, 0·1*N* oxalic acid and in solutions of NaCl, KCl, LiCl, NH_4Cl, $BaCl_2$, $CaCl_2$ and $MgCl_2$.

Determination of exchange capacity

The exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by a neutral salt, is found to depend upon the concentration and volume of the eluent for column operation. Therefore, to determine the most suitable concentration and volume, the elution curves of the hydrogen ion were found for various concentrations of eluent. The hydrogen ion eluted from the column was titrimetrically determined, with Methyl Orange as indicator. The results obtained with 0·1 and 1·0*M* sodium chloride are shown in Fig. 1. Although the hydrogen ions were still liberated even after

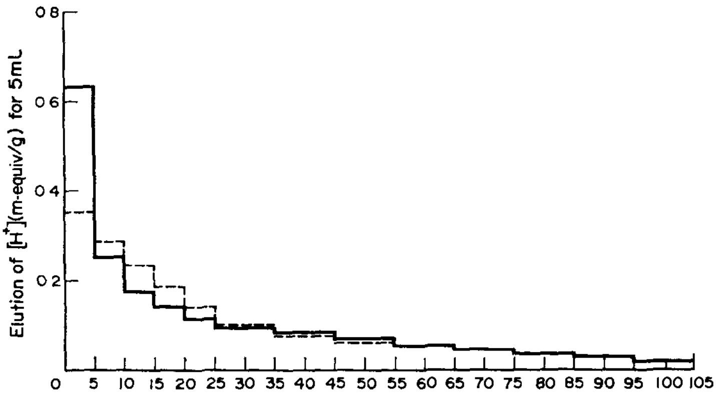


FIG. 1.—Elution curve of hydrogen ion. Continuous line—eluent 1·0*M* NaCl; dotted line—eluent 0·1*M* NaCl.

passage of 100 ml of the eluent, the exchange capacity was calculated from the amount of hydrogen ions liberated by 100 ml. The effect of concentration of neutral salt and time of equilibration on exchange capacity in batch operation, determined by the standard method,[9] is shown in Figs. 2 and 3, respectively. These studies were done on the typical sample 5A.

A constant value was obtained for concentrations of sodium chloride solution greater than 1*M* and it required practically 48 hr for complete equilibration. The capacity of different samples (H^+ form) is tabulated in (Table I), as is the value of hydrogen absorption capacity of different samples in Na^+ form. For checking the reproducibility of the method, the capacity of different samples from the same batch was determined for Na^+ ion. It shows a standard deviation of ±0.02. The batch reproducibility was checked by measuring the capacity of samples from different batches. It shows a standard deviation of ±0·038. The exchange capacity for Na^+ ion varies very little with initial pH (~ ±10%).

Since the sample 5A has the highest exchange capacity, the effect of the size and charge of the exchanging ion was studied with this sample only (Table II), as was the effect of drying temperature on exchange capacity (Table III).

The change of hydrogen liberation capacity in the course of regeneration cycles (Table IV) was studied for up to 6 cycles with different concentration of hydrochloric acid as regenerant.

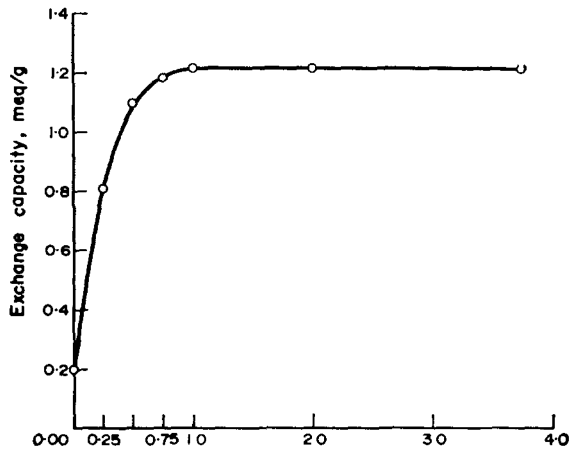


FIG. 2.—Exchange capacity of ceric antimonate (5A) as a function of concentration of Na^+.

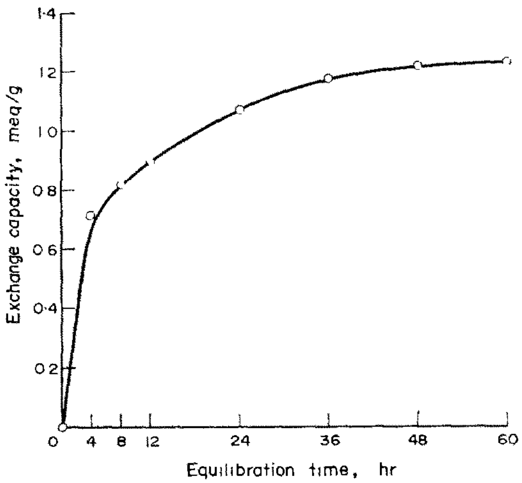


FIG. 3.—Effect of time of equilibration on exchange capacity of ceric antimonate (5A).

TABLE II.—EFFECT OF SIZE AND CHARGE OF EXCHANGING ION ON THE CAPACITY OF SAMPLE 5A.

Exchanging ion	Exchange capacity of ceric antimonate, *meq/g*
Li^+	0·91
Na^+	1·22
NH_4^+	1·25
K^+	1·27
Ba^{2+}	0·95
Ca^{2+}	1·20

TABLE III.—EFFECT OF DRYING TEMPERATURE ON EXCHANGE CAPACITY OF SAMPLE 5A.

Drying temperature, °C	Capacity, *meq/g*
14 ± 3	1·22
50	1·19
100	1·18
200	0·86
300	0·49
400	0·36

TABLE IV.—THE CHANGE OF CAPACITY IN THE COURSE OF ABSORPTION—REGENERATION CYCLES.

Cycle	Hydrogen liberation capacity	
	Regenerant 1·5*M* HCl eluent 1·0*M* NaCl	Regenerant 2·0*M* HCl eluent 1·0*M* NaCl
1	1·22	1·24
2	1·19	1·22
3	1·17	1·20
4	1·17	1·19
5	1·14	1·17
6	1·10	1·12

TABLE V.—DISTRIBUTION COEFFICIENTS FOR SOME CATIONS ON CERIC ANTIMONATE.

Cation	Taken as	K_d, *ml/g*
Tl(I)	Nitrate	26·3
Hg(II)	Nitrate	898
Zn(II)	Nitrate	23·3
Cd(II)	Sulphate	56·2
Co(II)	Nitrate	31·6
Ni(II)	Sulphate	3·8
Mn(II)	Sulphate	1·0
Mg(II)	Sulphate	19·2
Ba(II)	Nitrate	6·1
Ca(II)	Nitrate	7·6
Cu(II)	Sulphate	27·1
Pb(II)	Nitrate	23·7
Tl(III)	Nitrate	18·6
Al(III)	Sulphate	6·7
Fe(III)	Nitrate	94·8
Cr(III)	Nitrate	18·5
La(III)	Nitrate	3·2
Th(IV)	Nitrate	3·8
Zr(IV)	Nitrate	80·0
UO_2^{2+}	Acetate	22·2

Distribution coefficient

Distribution coefficients of metal ions were determined by batch operation, by radiometric, spectrophotometric and complexometric titration methods. About 100 mg of the exchanger (sample 5A) was loaded with 20 ml of 0·005*M* metal ion solution. The initial pH of the metal solution was adjusted to 2–3 with perchloric acid. The results are reported in Table V.

Separation of Hg^{2+} from Cd^{2+}, Zn^{2+}, Pb^{2+} and Tl^{+} was carried out in a column (5·0 cm × 0·19 cm^2) containing 50–100 mesh ceric antimonate. The column was loaded with 20% of the breakthrough capacity for each metal ion and the elution was started after 20 min at a flow-rate of ~0·15 ml/min. Cd^{2+}, Zn^{2+}, Pb^{2+} and Tl^{+} were separately eluted with water; Hg^{2+}, which remained on the exchanger, was then eluted with 0·5*M* NH_4Cl + 0·1*M* HCl (Fig. 4). Separations of Cu^{2+} from Mn^{2+}, Fe^{3+} from Al^{3+} and Zr^{4+} from Th^{4+} were carried out in a column 8·6 cm × 0·19 cm^2 (Fig. 5).

RESULTS AND DISCUSSION

The initial pH of the ceric solution is observed to have an effect on the exchange capacity of the products. With decreasing pH values higher exchange capacity is obtained. The pH of investigation was limited to between 0·75 and 2, since it is not possible to obtain a good product below pH 0·75 and above pH 2 cerium(IV) starts hydrolysing. The samples obtained with potassium pyroantimonate are not suitable for column operation, whereas those obtained with antimonic acid can be conveniently used in columns. The latter not only have better particle size but also a higher exchange capacity. The ratio and concentration of the mixing reagents seem to have negligible effect on the composition of the exchanger and its ion-exchange capacity.

The exchanger is apparently stable in water, alcohol, benzene, acetic acid, alkali solutions, different electrolyte solutions and mineral acids. Therefore, it can be used in these media without suffering deterioration in ion-exchange properties or break down of the particles.

As regards the effect of concentration of the neutral salt and the time of equilibration on capacity determination by batch operation, a constant value of the capacity for Na^+ ion was obtained at 1*M* or higher concentration, after 48 hr of equilibration.

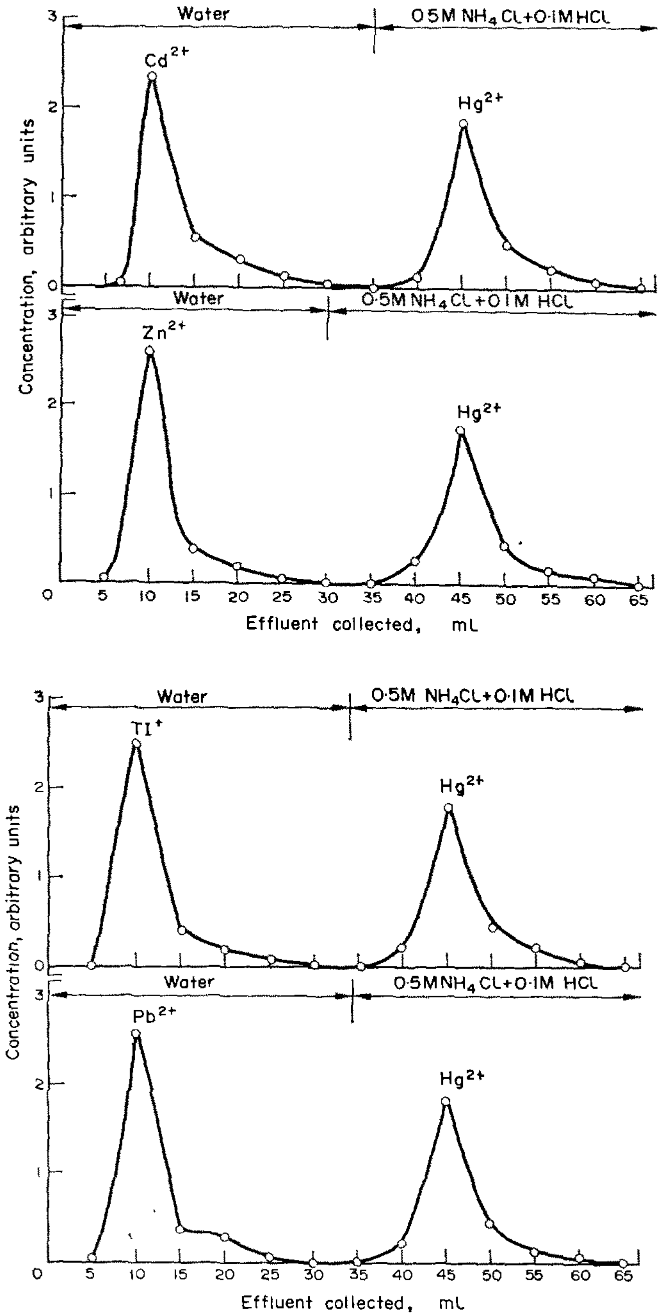


FIG. 4.—Separations on ceric antimonate column 5·0 cm × 0·19 cm^2, flow-rate ~0·15 ml/min.

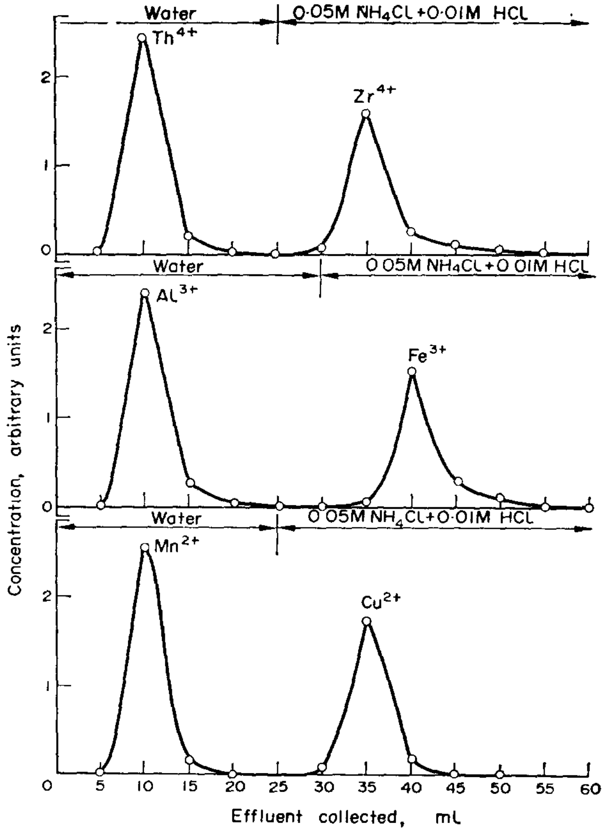


FIG. 5.—Separations on ceric antimonate column 8·6 cm × 0·19 cm², flow-rate ~0·15 ml/min.

Elution curves also reveal that at least 100 ml of 1*M* effluent is required for experimentally complete elution. The release of H^+ ions in the beginning is fast, then sharply decreases, and finally becomes insignificant after 100 ml of effluent. After 100 ml, it is not practical to continue the elution. The effect of pH on exchange capacity is practically negligible. Ceric antimonate in the acid form gives a buffer system of pH 2–3 and its exchange capacity remains unaltered at temperatures up to 100°. This suggests its possible use for buffering aqueous systems at higher temperatures. The exchange capacity seems to be negligibly affected by the size and charge of the exchanging ion, except for Li^+ and Ba^{2+} which show comparatively lower exchange capacity. The exchanger has a fairly good regeneration power.

The K_d values suggest the exchanger to be partly specific for Hg^{2+} ions and to provide a good method for its separation from other closely associated metal ions. Other separations of analytical importance have also been found possible.

Acknowledgement—The authors are grateful to Professor W. U. Malik, Head of the Chemistry Department, for research facilities. The financial assistance of C.S.I.R. (U.P.) and U.G.C. (India) is gratefully acknowledged.

Zusammenfassung—Cer(IV)-antimonat wurde unter verschiedenen Fällungsbedingungen hergestellt. Seine Eigenschaften und sein Ionenaustauschverhalten wurden untersucht. Mit diesem Material wurden Hg^{2+} von Zn^{2+}, Cd^{2+}, Pb^{2+} und Tl^{+}; Cu^{2+} von Mn^{2+}; Fe^{3+} von Al^{3+} sowie Zr^{4+} von Th^{4+} getrennt.

Résumé—On a préparé l'antimoniate cérique dans des conditions de précipitation variables. On a étudié ses propriétés et son comportement à l'échange d'ions. On a réalisé avec ce produit les séparations de Hg^{2+} de Zn^{2+}, Cd^{2+}, Pb^{2+}, et Tl^{+}; Cu^{2+} de Mn^{2+}; Fe^{3+} de Al^{3+}; et Zr^{4+} de Th^{4+}.

REFERENCES

1. C. B. Amphlett, *Inorganic Ion Exchangers*, Elsevier, Amsterdam, 1964.
2. H. O. Phillips and K. A. Kraus, *J. Am. Chem. Soc.*, 1962, **84**, 2267.
3. Gr. Popa, Gh. Baiulescu and S. Moldoveanu, *Rev. Chim. (Bucharest)*, 1960, **17**, 103.
4. M. Abe and T. J. Ito, *Kogyo Kogaku Zasshi*, 1967, **70**, 440.
5. J. S. Gill and S. N. Tandon, Unpublished work.
6. *Idem*, *J. inorg. Nucl. Chem.*, in the press.
7. H. L. Greenhaus, A. M. Feibush and L. Gordon, *Anal. Chem.*, 1967, **29**, 1531.
8. G. B. S. Salaria, *Anal. Chim. Acta*, 1957, **17**, 395.
9. O. Samuelson, *Ion Exchange Separation in Analytical Chemistry*, pp. 34–36. J. Wiley, New York, 1963.

Talanta, 1972, Vol. 19, pp. 1363 to 1375. Pergamon Press. Printed in Northern Ireland

DETERMINATION OF TRACE METALS IN WATER USING X-RAY FLUORESCENCE SPECTROMETRY

H. WATANABE,* S. BERMAN and D. S. RUSSELL
Division of Chemistry, National Research Council of Canada,
Ottawa, Ontario, Canada

(*Received* 21 *December* 1971 *Accepted* 8 *March* 1972)

Summary—A simple, rapid and accurate method for water analysis is proposed. The analytical procedure for the determination of Fe, Mn, Zn, Cu, Cd, As, Pb and Se in water in concentrations as low as a few ppM involves precipitation with a carrier of the metals by diethyldithiocarbamate (DDTC) or 1-(2-pyridylazo)-2-naphthol (PAN) and filtration through a Millipore filter. The precipitates collected on the filter disc are examined by X-ray fluorescence analysis. PAN is excellent for the determination of several metal ions at the ppM level, and DDTC can be used with tartrate as a masking agent if water samples contain large amounts of iron(III).

A LABORATORY engaged in making a large number of determinations of trace elements has a particular need for a rapid, simple and accurate method of analysis, especially in the field of quality control of natural waters. In this field, many spectrophotometric and atomic-absorption spectrometric methods are currently used. They are excellent for the determination of specific elements but they usually do not permit the simultaneous determination of several elements in water and they also lack sensitivity in the determination of trace metals below the 0·1 ppm level. Very few analytical methods allow the determination of several elements in microgram amounts in a single concentrate from water samples.

Neutron-activation, optical-emission and mass-spectrographic analysis have been successfully employed for the simultaneous determination of trace elements but these are time-consuming methods and their precision is rather poor. The X-ray fluorescence spectrometric method is excellent for the simultaneous determination of metals if a simple preparation of samples for X-ray measurement is established. Although this method has seldom been applied to water analysis, owing to its apparently low sensitivity, several workers have attempted to improve this sensitivity by developing a suitable method in which the trace elements are isolated before the X-ray analysis, using some physical or chemical method of separation,[1–7] including evaporation, precipitation, ion-exchange and solvent extraction.

Luke[8] and Püschel[9,10] have already reported that the precipitation of trace elements with some organic chelating reagents from water and the subsequent quick filtration of the precipitates with a Millipore filter were excellent for the determination of trace elements. Luke[8] has established the conditions for the determination of many trace metal ions with sodium diethyldithiocarbamate (DDTC), and Püschel[9] has recommended 1-(2-pyridylazo)-2-naphthol (PAN) as a precipitant. Such a chelating reagent, which forms insoluble metal chelates, can be used to recover the trace elements from water by isolating the trace elements as a thin uniformly dispersed precipitate in a low atomic-number matrix of relatively large area. The matrix absorption and enhancement are virtually negligible and hence the accuracy and the sensitivity of the

---

* Present address: Muroran Institute of Technology, Muroran, Hokkaido, Japan.

analysis is high. A single paper disc could permit the determination of several trace elements simultaneously.

In the present study (based on the works of Luke and Püschel) an attempt was made to establish a practical method for the simultaneous determination of several elements such as Fe, Mn, Cu, Zn, Cd, Pb, As and Se, which are always encountered in water analysis. The results clearly show that the X-ray method can be successfully applied to the determination of metal ions at ppM levels in water. The method is simple, rapid and sensitive.

EXPERIMENTAL

Apparatus

A Philips Universal Vacuum Spectrograph Model PW-1540/05 was employed. A chromium-target, thin-window X-ray tube operated at 50 kV and 28 mA was used in the determination of cadmium. A tungsten-target tube operated at 50 kV and 50 mA was used for all other elements tested. An EDDT analysing crystal was employed for cadmium and an LiF(220) crystal was used for the other metals. The diffracted radiation at each characteristic angle was measured with a gas-flow proportional counter, operated at about 2100 V in conjunction with pulse amplitude discrimination (Philips Pulse Height Amplifier, Model PW 4280) optimized for each element.

The filter equipment was the same as described by Luke.[8] It consists of a Pyrex filter holder supplied by the Millipore Corporation of Bedford, Mass. and includes a reservoir, a 17-mm circular fritted glass support and a metal clamp. The filter paper discs used were white 25-mm Millipore paper discs of 1·2 μm pore size. After insertion of the disc and clamping on of the reservoir, the solution was filtered under suction. The paper disc was held between two aluminium rings to prevent curling up on drying in an oven at 100°, and was then mounted in an aluminium sample holder that had a Mylar-film base through which the primary X-ray beam irradiated the precipitates on the paper disc. A pressed disc of pure cellulose, which had a diameter slightly smaller than the inside diameter of the aluminium holder and had a thickness of 5 mm, was inserted into the holder to keep the disc flat.

Reagents

Metal ion solutions were prepared from high purity metals or metal oxides ($<0{\cdot}001\%$ impurity). They were dissolved in an appropriate acid solution and then diluted with doubly distilled water to the desired concentration. The final acidity of the solutions was about $0{\cdot}11N$. Other reagents used were of analytical grade. Several buffer solutions were prepared[11] and purified by the following precipitation method: 100–200 μg of copper and 50 mg of DDTC were added to the buffer solution, and the precipitates formed were removed by filtering through a Millipore filter. Both the citrate and the tartrate solutions were purified in the same manner. The buffer solution of pH 10 prepared from ammonia and ammonium chloride was purified with a chloroform solution of PAN. PAN itself was purified by dissolving in chloroform and washing the solution with $0{\cdot}01M$ EDTA solution at pH 10 and with doubly distilled water. The chloroform was then evaporated.

All glassware, beakers and pipettes were immersed in nitric acid (1 + 1) and washed with doubly distilled water before use.

Procedure

In most experiments 50 ml of sample solution were transferred to a beaker and 5 ml of 2% DDTC solution (freshly prepared and filtered) were added. The acidity of the solution was adjusted with a buffer solution, and if necessary with suitable amounts of hydrochloric acid or sodium hydroxide solution. The precipitate was allowed to stand for 5 min and filtered off on the Millipore filter. When PAN was used as a precipitant the sample solution was gently boiled for about 20 min on a hot-plate after the addition of 0·1% methanol solution of PAN and of pH 10 buffer solution. PAN chelates tend to float on the surface of the solutions and climb up the wall of the beaker, so several drops of surfactant solution (1% sodium lauryl sulphate) were added.

The intensity of each characteristic line was measured for 1 min except for cadmium, lead, arsenic(III) and selenium, which were counted for 2 min. Both sample and spectrometer chambers were evacuated to a pressure of less than 0·5 mmHg. The analytical lines used for X-ray measurement are summarized in Table I.

TABLE I.—LINES USED IN X-RAY MEASUREMENTS.*

Element	2θ angle	
	Peak	Background
Mn	K_α 95·19°	97·00°
Fe	K_α 85·71°	87·00°
Cu	K_α 65·54°	65·54°
Zn	K_α 60·56°	60·56°
Cd	$L_{\alpha 1}$ 53·41°	54·40° 52·40°
As	K_α 48·78°	47·80° 49·80°
Pb	$L_{\alpha 1}$ 48·73°	47·90° 49·56°
Se	K_α 45·70°	45·70°

* LiF analysing crystal, tungsten target (w), except for Cd, where an EDDT crystal and a chromium target were used.

RESULTS

DDTC as precipitant

In water analysis the following metal ions are most often determined: Fe, Mn, Cu, Zn, Cd, Pb, As and Se. For the precipitation of these elements in one step a rather non-specific organic reagent must be used. Among the precipitants that have been investigated DDTC would appear to be a good choice. The results obtained by Luke were confirmed for the precipitation of the elements Fe, Cu, Zn, Cd, Ni, Pb and Mn, atomic-absorption spectrometry being used to examine the filtrates. Nickel and copper were precipitated completely between pH 1 and 11. Zinc, cadmium, lead and iron(III) began to precipitate at pH 1–2 and precipitation was complete at pH above 4. Thus the pH of the solution should be kept above 4, and in the present work pH 5 was chosen. However, unsatisfactory results were obtained with manganese, over the whole pH range examined, because of incomplete precipitation. The recovery of manganese was improved by the addition of 50 μg of copper as a co-precipitant but recovery was never complete. Therefore the use of DDTC is unsuitable for the determination of manganese. Luke has recommended the use of 50 μg of copper or 100 μg of iron(III) as the co-precipitants at pH 9 for the recovery of manganese; however, both iron and copper are always primary elements to be determined in water analysis, which precludes their use.

The recovery of arsenic(III) was examined by using X-ray fluorescence. The results are shown in Fig. 1, where the ordinate is the ratio of the counts obtained at various pH values to those obtained at pH 5·0. Luke[8] reported that the recovery of arsenic(III) as the diethyldithiocarbamate was quantitative only at pH 4. However, these results indicate that the pH for arsenic(III) must be in the range 5·0–5.5. Therefore, in this experiment pH 5·1 was chosen for the precipitation of arsenic(III).

Calibration curves. On the basis of the results described above calibration curves were made by precipitating and determining from 0 to 50 μg of each of the elements.

Over the range examined, a linear relationship was obtained between the amount of element taken and the ratio obtained by dividing the net count of each sample by that of a reference sample. The reference chosen was the median of eleven samples

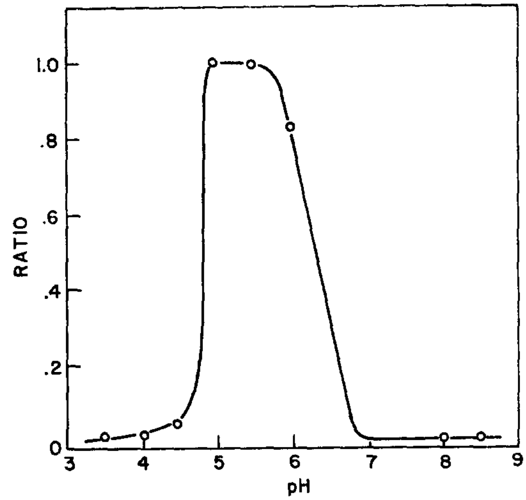


FIG. 1.—Influence of pH on the recovery of 5 μg of As(III) with DDTC, expressed as the ratio of the intensity determined at various pH values to that determined at pH 5·0.

examined over the concentration range. This linearity suggests the complete precipitation of each element. On the basis of these calibration curves the 95% confidence limit was calculated by the least-squares method, for the sample with concentration C yielding a ratio $R = 1$. The results are shown in Table II. The limit of detection at the 95% confidence level, D, was calculated from the relationship $D \sim 3C\sqrt{B}/M$, where M is the slope of the calibration curve and B the background intensity based on a 2-min counting period.[12] The backgrounds for zinc and selenium were determined by making measurements on blank samples at the appropriate line peak. From this table it is seen that the precision of this method is quite good. Five μg of Fe, Zn, Cd and Cu can be determined with a precision of ±0·3 μg. If 50 ml of solution contains 5 μg of an element it is then possible to determine 0·1 ppm of the element to within ±0·006 ppm.

TABLE II.—SENSITIVITY AND PRECISION USING DDTC.

Element	Carrier	Sensitivity, *counts/sec/ μg*	Background, *counts/sec*	Limit of detection, *μg*	95% confidence limit of C for $R^* = 1·0$, *μg*
Fe	Cu	98	129	0·03	5·15 ± 0·25
Zn	Cu	72	182	0·05	5·47 ± 0·30
Cd	Cu	25	34	0·06	5·18 ± 0·06
Zn	Ni	58	194	0·06	5·10 ± 0·34
Fe	Ni	102	101	0·03	5·26 ± 0·36
Cu	Ni	99	400	0·06	6·08 ± 0·35
Pb	Ni	19	51	0·10	25·10 ± 0·28
As	Ni	20	50	0·10	20·30 ± 0·20
Se	Ni	19	72	0·12	25·05 ± 0·60

* $R = a + bC$; R represents the ratio of determined intensity to that of the reference standard, and C the concentration.

Two calibration curves for zinc were established, for two sample sizes, 50 ml and 250 ml. In both cases a linear relationship and the same slope were obtained.

The precision can be expressed in concentration terms for the samples containing 5 μg of zinc as follows: 50 ml sample—0·1 ± 0·006 ppm, 250 ml sample—0·02 ± 0·0015 ppm. It is apparent from Table II that cadmium can be determined with the greatest accuracy. This is probably due to the low background in the vicinity of the cadmium $L_{\alpha 1}$ line.

As shown in Table II, satisfactory results were also obtained for the determination of arsenic(III), selenium(IV) and lead. Unfortunately their sensitivities are inferior to those of the the other elements.

Copper or nickel was used as the carrier metal ion in these experiments. There seems to be a slight difference in their efficiencies. Since copper is an important element in water analysis, nickel is recommended as the carrier element.

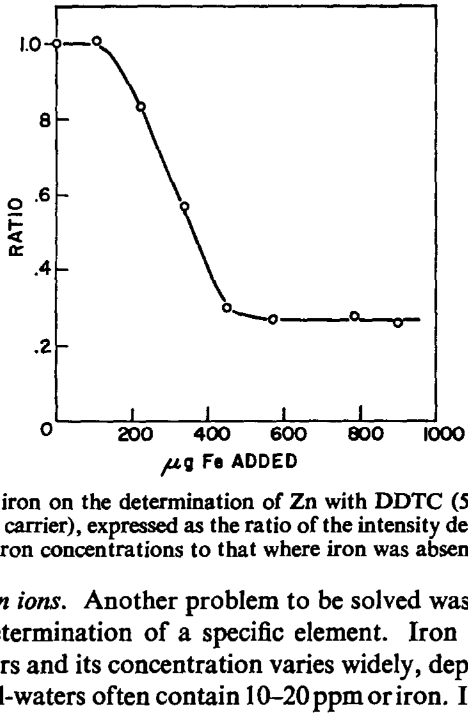


FIG. 2.—Effect of iron on the determination of Zn with DDTC (5 μg of Zn, pH 5·0, 50 μg of copper as carrier), expressed as the ratio of the intensity determined at various iron concentrations to that where iron was absent.

Influence of foreign ions. Another problem to be solved was the influence of other metal ions on the determination of a specific element. Iron is a common element found in natural waters and its concentration varies widely, depending on the geological locality. Some well-waters often contain 10–20 ppm or iron. If the method described here is used directly for the analysis of such waters the result will be erroneous because the precipitate will be too thick. This was tested on solutions containing 5 μg of zinc, 50 μg of copper and various amounts of iron(III). In Fig. 2, the ordinate shows the ratio between the net count of samples containing various amounts of iron(III) and that of the reference which contains no iron. Iron clearly interferes if large amounts of iron co-exist, but quantities up to 100 μg can be tolerated without appreciable error in the determination of zinc. Assuming 50 ml of sample solution, the concentration of iron should be below 2 ppm.

The determination of arsenic (III) is influenced by the presence of lead, and *vice versa*. The K_α line of arsenic(III) appears at the same 2θ angle as the $L_{\alpha 1}$ line of lead, as shown in Table I, making it impossible to identify and determine both elements simultaneously. However the separation of both elements is feasible, as discussed later.

Masking of iron(III). The concentration of iron in most river waters is usually below 2 ppm. For higher iron concentrations this method cannot be applied without some modifications. Iron could be separated before the analysis, but it was considered impractical to do so because the analytical procedure would lose its simplicity and rapidity. Thus, the only remaining approach was to mask the iron, thereby avoiding the addition of other analytical steps.

When copper is determined with DDTC, it is well-known that EDTA has strong complexing abilities with respect to iron(III), manganese, zinc and cadmium,[13] making it possible to separate these elements from copper. Therefore EDTA cannot be used for the determination of zinc and cadmium in the presence of iron. In the next experiment it was confirmed that iron(III) is masked with tartrate or citrate,[13] while zinc and cadmium are precipitated in the presence of these reagents. The influence of tartrate and citrate on the precipitation of zinc, cadmium and iron(III) is shown in Figs. 3 and 4 (atomic-absorption spectroscopy was used to determine the metal ions in a filtrate). This effect was confirmed by the examination of the precipitated metals by X-ray fluorescence. The recovery of zinc was also examined in the presence of 0·05*M* tartrate and various amounts of iron(III) (Fig. 5). Tartrate increases the tolerance for iron tenfold. Under the same conditions cadmium is also quantitatively precipitated although it is not shown here. Thus, if 50 ml of sample are taken, 20 ppm of iron(III) could be tolerated in the determination of zinc and cadmium. A borate buffer solution must be used for adjusting the pH of the solution to 9·5 or higher. Experiments showed that up to 275 μg of copper, 250 μg of manganese and 40 mg of calcium could be tolerated without any appreciable effect on the recovery of zinc.

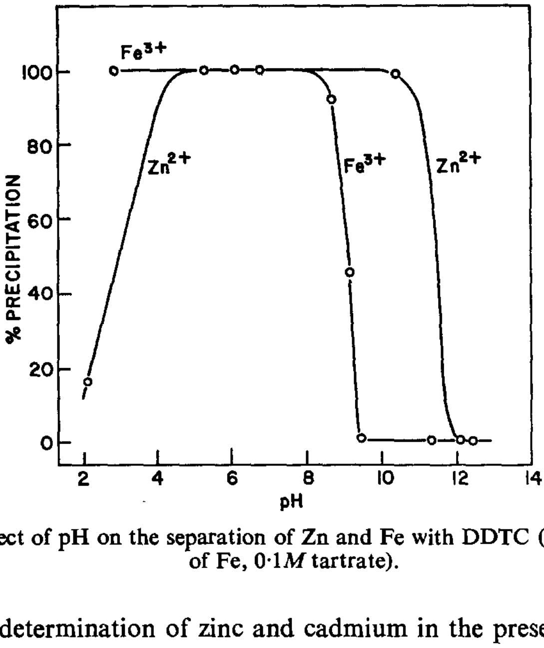


FIG. 3.—Effect of pH on the separation of Zn and Fe with DDTC (5 μg of Zn, 5 μg of Fe, 0·1*M* tartrate).

In Table III the influence of nickel on the recovery of Cd, Zn and Cu is also shown. Quantities of nickel below 100 μg have no effect on the determination of these elements

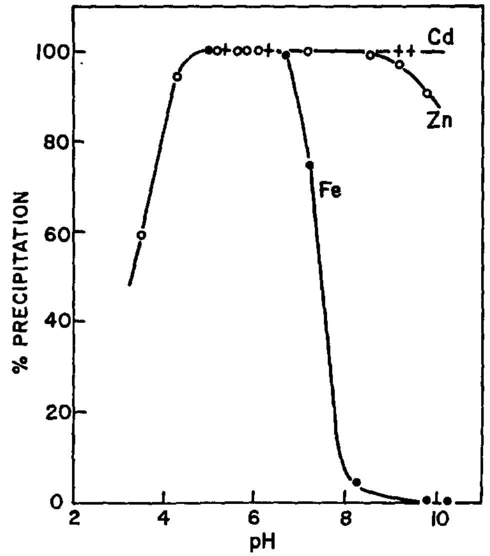


Fig. 4.—Effect of pH on the separation of Fe from Zn and Cd with DDTC (5 µg of Zn, 5 µg of Fe, 5 µg of Cd, 0·1*M* citrate).

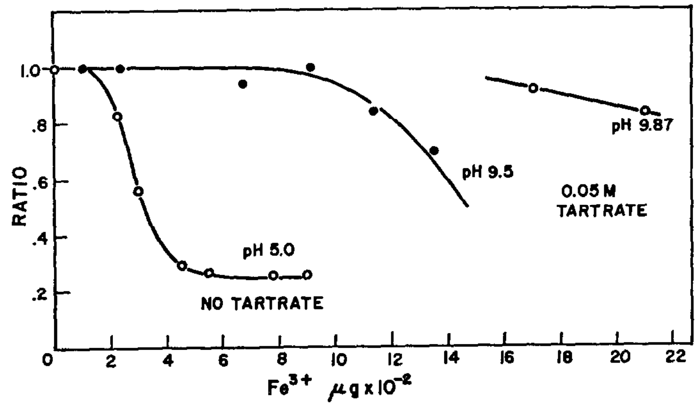


Fig. 5.—Recovery of Zn with DDTC in tartrate solutions (5 µg of Zn, 50 µg of copper as carrier).

Table III.—Influence of Ni on the determination of 5 µg of Cd, Zn and Cu with DDTC (in 50 ml).

Element	Ratio		
	Ni added, µg		
	50	100	200
Cd	1·00	1·01	0·66
Zn	1·00	1·02	1·04
Cu	1·00	0·98	0·94

and hence the amounts of copper or nickel to be added as a carrier do not have to be precise. Sodium, calcium and magnesium are always found in natural water but as they do not react with DDTC no interference would be expected.

When the concentration of iron is very high the simultaneous determination of iron and other trace elements is impossible and the sample must be divided into two portions. Large amounts of iron can be determined by using a smaller sample.

It is generally accepted that citrate is a more powerful masking reagent for iron(III) than tartrate.[14] Zinc can be separated from iron(III) by using citrate, as shown in Fig. 4. The pH of the solution should be kept within the range 8–8·5. Under these conditions cadmium also can be completely isolated from iron(III). Therefore citrate could well be used as a masking reagent for iron as well as tartrate, but no further experiments were carried out.

Influence of sample volume. Table IV shows the influence of sample volume on the determination of cadmium and arsenic(III). It is apparent that the recovery of cadmium and arsenic decreases with increasing sample size and hence DDTC cannot be used with the nickel carrier for samples larger than 50 ml for Cd and 100 ml for As(III). However when copper is used as a carrier the cadmium can be recovered quantitatively from volumes up to 300 ml. Other experiments indicated that cadmium could be completely recovered from volumes up to 200 ml by using the nickel carrier if the time of precipitation was extended to 30 min before filtration. As shown in Table II, zinc was determined with good precision from a 250-ml sample. Although no further experiments were carried out on the recovery of lead and selenium, these form very stable complexes with DDTC.[1,13] The metal ions which form the most stable complexes with the precipitant are easily and completely recovered.

TABLE IV.—EFFECT OF SAMPLE VOLUME ON THE DETERMINATION OF CADMIUM AND ARSENIC(III) WITH DDTC.

	Sample size *ml*	Ni added, *μg*	Ratio
Cd 5·15 *μg*	50	50	1·00
	100	50	0·54
	500	50	0·18
	500	100	0·33
	300	*	0·98
As 20·3 *μg*	50	50	1·00
	100	50	1·01
	200	50	0·81
	300	50	0·24
	500	50	0·02

* Nickel replaced with 50 *μg* of copper as carrier.

PAN as a precipitant

As a non-specific organic reagent, PAN was proposed by Püschel[9] for the determination of trace metals by X-ray fluorescence. DDTC is an ineffective reagent for the determination of manganese and in this respect PAN is superior. The most suitable pH for the determination of Fe, Mn, Cu, Zn and Cd was 10. In the procedure of Püschel metal ions were precipitated as the metal–PAN complexes from about 20–60 ml of solution to which 3 ml of pH 10 buffer solution and 5 ml of 0·1%

methanolic PAN solution had been added. For the precipitation of less than 10 μg of metal ions in the presence of 50 μg of nickel, 1 ml of 0·1 % PAN solution was more than adequate.

However PAN has some undesirable properties. The first of these is that PAN itself is only slightly soluble in water and hence the excess of reagent is also recovered on filtration. This causes an increase in the volume of the precipitates and results in the cracking and peeling of the precipitates from the Millipore filter on drying. The second drawback is due to the properties of the precipitates formed. They often float on the surface of the solution and tend to adhere to the walls of the beaker, necessitating the addition of several drops of surfactant solution.

Calibration curves. To establish the calibration curves for each element, 1 ml of 0·1 % PAN solution was added to 50 ml of the sample solution, which contained 50 μg of nickel and 0–10 μg of one of the elements to be determined. The solution was adjusted to pH 10 with 3 ml of ammonia buffer and several ml of 1*M* sodium hydroxide. The solution was heated gently to boiling on a hot-plate for about 20 min to complete the reaction. The slower reaction of metal ions with PAN than with DDTC makes the analysis time longer.

In Table V the results of the calibration curves for the elements are summarized.

TABLE V.—SENSITIVITY AND PRECISION USING PAN WITH NICKEL CARRIER.

Element	Sensitivity, *counts/sec/ μg*	Background *counts/sec*	Limit of detection, *μg*	95 % confidence limit of *C* for $R^* = 1·0$, *μg*
Mn	69	42	0·03	5·15 ± 0 20
Cu	104	392	0 05	6·30 ± 0·16
Cd	32	34	0·05	5·05 ± 0·13
Fe	78	19	0·02	5·07 ± 0·26
Zn	30	25	0·05	5·11 ± 0·23

* $R = a + bC$; *R* represents the ratio of determined intensity to that of the reference standard, and *C* the concentration.

It is apparent that each element can be determined with PAN with a better precision than with DDTC.

Influence of foreign ions. At the 5-μg level, cadmium, zinc, copper and manganese were quantitatively recovered without a carrier. However only 95 % of the iron was recovered. When nickel was used as a co-precipitant all the metals were completely recovered although quantities larger than 100 μg of nickel reduced the net count for cadmium. Thus the nickel carrier should be below 100 μg. In fact the addition of less than 50 μg of nickel is recommended to improve the ease of filtration of precipitates.

The influence of other elements is shown in Table VI. It is evident that 100 μg of Fe, Mn or Cu, when present individually, do not cause interference but the total amount of these metals in an aliquot should be below 100 μg when PAN is used as the precipitant. At least 24 mg of calcium could be tolerated without interference.

Influence of masking reagents. The effect of some masking reagents is summarized in Table VII. It has already been reported[15] that PAN can be used as an extractive spectrophotometric reagent for the simultaneous determination of cobalt, nickel and iron in a slightly acid solution without any interference from other elements if EDTA is used as a masking reagent. However, in basic solution EDTA is not selective and

TABLE VI.—INFLUENCE OF SOME ELEMENTS ON THE DETERMINATION OF 5 μg EACH OF Fe, Mn, Cd, Zn AND Cu WITH PAN.

Element added, μg	Ratio				
	Zn	Cu	Fe	Mn	Cd
Reference	1·00	1·00	1·00	1·00	1·00
Fe 45	1·02	0·98		0·98	1·01
90	0·97	1·01		0·99	1·01
180	0·96	0·90		0·97	0·94
270	0·92	0·89		1·00	0·84
Mn 50	0·99	1·02	1·03		0·96
100	0·98	0·97	1·03		0·97
200	0·83	0·91	1·00		0·88
300	0·90	0·88	1·01		0·85
Cu 50	1·01		1·01	0·99	1·03
100	1·06		1·04	1·01	0·97
200	0·97		1·04	1·00	0·89
300	1·02		1·07	0·99	0·83

TABLE VII.—EFFECT OF SOME MASKING REAGENTS ON THE DETERMINATION OF 5 μg OF Cd, Zn, Mn AND Fe WITH PAN AT pH 10.

Masking reagents added	Ratio			
	Cd	Zn	Mn	Fe(III)
	1·00	1·00	1·00	1·00
TEA*, 0·054*M*	0·95	0·99	0·98	0·91
NTA†, 0·004*M*	0·43	0·014	0·004	0·88
Pyrophosphate, 0·0056*M*	0·99	0·87	0·103	0·94
Pyrophosphate, 0·0056*M* and TEA 0·054*M*	0·98	0·82	0·049	0·93
Tartrate, 0·02*M*	0·97	0·96	0·95	0·95
Citrate, 0·01*M*	1·01	1·00	0·60	0·89

* Triethanolamine.
† Nitrilotriacetic acid.

consequently cannot be used. Table VII shows that none of the reagents tested was effective in masking iron(III) since zinc and cadmium were also masked. In this respect PAN is inferior to DDTC.

Influence of sample size. A series of experiments was performed to determine the efficiency of the recovery from larger sample volumes, using 50 μg of nickel as carrier. It is interesting that copper, zinc and cadmium are completely recovered even from 1000 ml of solution. This means that less than one ppM of these metals can be determined if large aliquots are taken. In this respect PAN is superior to DDTC.

When the sample size is increased to 500 or 1000 ml the carrier must always be used, contrary to Püschel's recommendation that no carrier be used. Without a carrier, only 84% of the manganese and 89% of the iron was recovered from samples of 500 ml. This may be attributed to the low stability constants of the iron and manganese complexes with PAN.

Application of the method to water analysis

As a test of the method, a series of 25–200 ml portions of river water (Ottawa River) was analysed. The comparison of results obtained by using X-ray fluorescence, atomic-absorption and absorption spectrophotometry is given in Table VIII. The iron was determined colorimetrically with 1,10-phenanthroline, and the other metals were determined by atomic absorption after extraction with DDTC into methyl isobutyl ketone.[16] These results indicate that the proposed analytical method is satisfactory. All the water samples taken were acidified with 6*M* hydrochloric acid and gently boiled for 30 min before analysis.

TABLE VIII.—ANALYSIS OF OTTAWA RIVER WATER.

Method			μg/l			
			Cu	Fe	Mn	Zn
Absorption spectrophotometry		Raw*	—	162	—	—
		Effluent†	—	61	—	—
Atomic absorption		Raw	240	157	—	—
		Effluent	27	65	—	4·2
X-Ray	DDTC	Raw	235	165	—	—
		Effluent	30	59	—	4·0
	PAN	Raw	244	160	10·6	—
		Effluent	31	58	8·7	3·8

* Raw water at the inlet of a filtration plant.
† Effluent water at the outlet.

DISCUSSION

The X-ray method proposed here has certain advantages. Many current methods of water analysis do not permit the simultaneous determination of several metal ions and the sensitivity is comparatively low. Thus, for the determination of heavy metal ions at the ppM level some preconcentration must be carried out and solvent extraction has often been used for this purpose. In this respect, the same situation arises in the X-ray method, but the precipitation makes the procedure relatively so simple that the method established in this study has a wider applicability than others, especially in the determination of trace metals below 50 or 100 ppM in water.

Some workers have recommended ion-exchange[6,16] and solvent extraction[1,2] for preparing the X-ray sample, but these methods are not simple and are time-consuming because of the complexity of the preparation of films in which trace metals are isolated and concentrated.

In the present method some problems remain. One is in the X-ray working conditions for the determination of cadmium. For the measurement of the L_{α_1} line of cadmium, the chromium target and EDDT analysing crystal must be used, instead of the tungsten target and LiF(220) crystal, which are used for other elements. Since two different counting conditions must be utilized for cadmium and other elements, there is no possibility of determining cadmium simultaneously with other elements by a scanning technique. Another problem is the precipitant. Neither DDTC nor PAN can be used for the analysis of all kinds of waters. DDTC does not recover the trace elements from large samples and low ppM levels of metals cannot be determined. On the other hand, PAN cannot be applied to the samples containing large amounts of iron because there are no suitable reagents to mask iron and to permit the precipitation of zinc and cadmium.

There is a problem in the determination of arsenic(III) and lead because the K_α line of arsenic appears at the same 2θ angle as the L_{α_1} line of lead. To avoid the mutual line interference, both elements must be separated. The first method is based on the fact that PAN does not react with As(III). The lead–PAN complex can be recovered with other elements, except for selenium(IV), under the conditions indicated in the procedure. On the other hand, As(III) is not precipitated by DDTC in basic solution. As shown in Fig. 1, arsenic(III) precipitates only in the pH range 5·0–5·5 and it does not precipitate at above pH 7. Therefore, DDTC permits the recovery of lead at pH 9·5 as well as zinc and cadmium. Hence both elements could be isolated and determined independently if their concentration was at least 10 μg/l. Although DDTC can precipitate the seven elements, except manganese, at pH 5, two separate precipitations must be carried out in order to avoid the mutual line interference between lead and arsenic. If PAN is used as a precipitant, six elements (except arsenic and selenium) can be recovered at pH 10 and subsequently arsenic and selenium are precipitated from the filtrate with DDTC at 5·1. In both cases two precipitation steps are needed, especially when arsenic and lead must be determined.

It has already been reported by some workers[13] that the stabilities of the chelates of each element with DDTC increase in the order $\mathrm{Mn} < \mathrm{As(III)}$, $\mathrm{Zn} < \mathrm{Fe(III)} < \mathrm{Cd} < \mathrm{Pb} < \mathrm{Ni}$, $\mathrm{Co} < \mathrm{Cu}$. Hence, the reason for the incomplete recovery of manganese with DDTC must be attributed to the low stability of its chelate. The arsenic chelate with DDTC also exhibits low stability, thus arsenic(III) is also difficult to precipitate quantitatively, if the pH of the solution is not controlled precisely between pH 5·0 and 5·5. On the other hand, the precipitation of selenium(IV) is complete at pH 5. Although the influence of pH on the precipitation of selenium(IV) with DDTC was not examined in this experiment, Bode[17] has already reported that selenium(IV) could be extracted with DDTC into carbon tetrachloride at a pH between 4 and 6·2. The selenium complex with DDTC seems to have greater stability than that of arsenic(III).

Finally, it is concluded that the advantages of the method lie in its rapidity, simplicity, relatively good precision and general sensitivity, since the preparation of sample for X-ray measurement is simple and reproducible.

Zusammenfassung—Eine einfache, rasche und genaue Methode zur Wasseranalyse wird vorgeschlagen. Das analytische Verfahren zur Bestimmung von Fe, Mn, Zn, Cu, Cd, As, Pb und Se in Wasser bei Konzentrationen von einigen ppM besteht in einer Trägerfällung der Metalle mit Diäthyldithiocarbamat (DDTC) oder 1-(2-Pyridylazo)-2-naphthol (PAN) und Filtration durch ein Millipore-Filter. Der auf der Filterscheibe gesammelte Niederschlag wird mittels Röntgenfluoreszenz untersucht. PAN ist ausgezeichnet zur Bestimmung mehrerer Metallionen im ppM-Bereich geeignet und DDTC kann mit Tartrat als Maskierungsmittel benutzt werden, wenn das Wasser große Mengen Eisen(III) enthält.

Résumé—On propose une méthode simple, rapide et précise pour l'analyse de l'eau. La technique analytique pour le dosage de Fe, Mn, Zn, Cu, Cd, As, Pb et Se dans l'eau à des concentrations aussi faibles que quelques p.p.m. comprend la précipitation des métaux avec un entraîneur par le diéthyldithiocarbamate (DDTC) ou le 1-(2-pyridylazo) 2-naphtol (PAN) et la filtration sur un filtre Millipore. Les précipités recueillis sur le disque de filtre sont examinés par analyse de fluorescence aux rayons X. Le PAN est excellent pour le dosage de plusieurs ions métalliques au niveau de la p.p.m., et l'on peut utiliser le DDTC avec le tartrate comme agent dissimulant si les échantillons d'eau contiennent de grandes quantités de fer(III).

REFERENCES

1. F. J. Marcie, *Environ. Sci. Technol.*, 1967, **1**, 164.
2. A. W. Morris, *Anal. Chim. Acta*, 1968, **42**, 397.
3. K. Haberer, *Vom Wasser*, 1965, **17**, 128.
4. S. Natelson, D. R. Leighton and O. Calas, *Microchem. J.*, 1962, **6**, 539.
5. S. L. Tackett and M. A. Brocious, *Anal. Letters*, 1969, **2**, 649.
6. J. P. Riley and D. Taylor, *Anal. Chim. Acta.* 1968, **40**, 479.
7. Y. K. Park, *Daehan Hwahok Hwoe*, 1969, **13**, 45; *Chem. Abstr.*, 1970, **72**, 24460 n.
8. C. L. Luke, *Anal. Chim. Acta*, 1968, **41**, 237.
9. R. Püschel, *Talanta*, 1969, **16**, 351.
10. *Idem*, *J. Less-Common Metals*, 1969, **19**, 313.
11. L. Meites, *Handbook of Analytical Chemistry*, pp. 11–16. McGraw-Hill, New York, 1963.
12. S. S. Berman, P. Semeniuk and D. S. Russell, *Can. Spectry.*, 1969, **14**, 3.
13. A. Hulanicki, *Talanta*, 1967, **14**, 1371.
14. D. D. Perrin, *Masking and Demasking of Chemical Reactions*, p. 161. Wiley-Interscience, New York, 1970.
15. R. Püschel, E. Lassner and K. Katzengruber, *Z. Anal. Chem.*, 1966, **223**, 414.
16. H. Taylor and F. E. Beamish, *Talanta*, 1968, **15**, 497.
17. H. Bode, *Z. Anal. Chem.*, 1955, **144**, 165.
18. J. F. Nix and T. Goodwin, *At. Absorption Newsletter*, 1970, **9**, 119.

Talanta, 1972, Vol. 19, pp. 1377 to 1386. Pergamon Press. Printed in Northern Ireland

STUDIES ON CHROMIUM(III) HYDROXIDE, ARSENATE, ANTIMONATE, MOLYBDATE AND TUNGSTATE

MOHSIN QURESHI, RAJENDRA KUMAR and H. S. RATHORE
Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P., India

(*Received* 5 *November* 1971. *Accepted* 5 *April* 1972)

Summary—Five water-insoluble compounds of chromium(III) have been synthesized by mixing 0·10*M* solutions of chromic chloride and the appropriate sodium salts in the volume ratio of 1:2, at pH 6–7. Their ion-exchange characteristics have been compared. The tungstate has the highest chemical stability and the arsenate has the highest ion-exchange capacity. Chromium(III) molybdate columns have been used to separate Pb^{2+} from numerous metal ions.

NUMEROUS ion-exchangers have been synthesized and the mechanism[1,2] of separation has been studied for some of them. The ion-exchange properties of a material are considerably influenced by the chemical composition of the ion-exchanger.[3] They also depend on the method and the conditions of preparation. It is therefore not always possible to compare the ion-exchange properties of the same materials synthesized in different laboratories and it would be interesting and instructive to prepare inorganic ion-exchangers with the same cation but with different anions and to compare different preparations. Szirtes *et al.*[4] made a comparative study of zirconium, titanium and chromium phosphates. While our work on stannic arsenate was in progress we noticed that chromium(III) is irreversibly adsorbed on stannic arsenate.[5] We therefore decided to synthesize chromium(III) arsenate and to compare its ion-exchange properties with other insoluble compounds of chromium(III). The present paper summarizes the results of such a study.

EXPERIMENTAL

Reagents

Chromic chloride hexahydrate, sodium molybdate, sodium tungstate and sodium arsenate heptahydrate were used. Antimony pentachloride solution (s.g. 2·30) was diluted with 4*M* hydrochloric acid to obtain solutions of the required concentration. All other reagents were of analytical grade.

Apparatus

A Philips conductivity bridge PR 9500, Sargent Oscillometer type (V) and Aminco thermoanalyser were used for conductimetry, high frequency titrations, DTA and TG respectively. All other instruments were those used in our earlier studies.[6,7]

Preparation

The chromium(III) compounds have been synthesized under similar conditions to facilitate comparison (Table I). The reagents given in column 2 were mixed in the volume ratios given in column 3. The pH of the reaction mixture was found to be 6–7 in the case of arsenate, molybdate and tungstate, and was adjusted to 6·80 in the case of antimonate by adding ammonia solution dropwise with constant shaking. Chromium hydroxide has also been prepared by adding ammonia solution to aqueous 0·10*M* chromic chloride. The gelatinous precipitates obtained were washed by decantation, filtered off, washed again with distilled water and then dried at 40°. Aging always affects the properties of this type of inorganic ion exchanger.[8] Therefore all the precipitates were kept for 24 hr with reaction mixture at room temperature. The dried product was immersed in 1*M* nitric acid (approximately 40 g of the exchanger in 100 ml of 1*M* nitric acid) to remove the foreign ions adsorbed during the preparation. Some dissolution of the compound was observed during this process. Finally the exchangers were washed with demineralized water to remove the excess of acid and again dried at 40°.

TABLE I.—SYNTHESIS AND PROPERTIES OF HYDROXIDE, ARSENATE, ANTIMONATE, MOLYBDATE AND TUNGSTATE OF CHROMIUM(III).

Compounds	Conditions of synthesis			Properties								
	Reagent used	Mixing volume ratio	pH	Colour in H^+ form			I.E.C. *meq/g.* for K^+ at pH 6–7			Composition Cr:X		
				40°	200°	500°	40°	200°	500°	H.F.	C.M.	C.A.
1. CrOH	0·10*M* $CrCl_3·6H_2O$	—	—	GBl	DG	DG	0·00	0·00	0·00	—	—	—
2. CrAs	0·10*M* $CrCl_3·6H_2O$ 0·10*M* $NaHAsO_4·7H_2O$	1:2	7·00	LG	LG	Gr	0·63	0·64	0·26	1:2·10	1:2·10	1:1·98
3. CrSb	0·10*M* $CrCl_3·6H_2O$ 0·10*M* $SbCl_5$(in 4M HCl)	1:2	6·80	SBl	GBl	B	0·42	0·46	0·22	—	—	1:2·95
4. CrMo	0·10*M* $CrCl_3·6H_2O$ 0·10*M* $Na_2MoO_4·2H_2O$	1:2	6·10	ShGB	ShStGr	ShB	0·34	0·01	0·00	1:1·82	1:1·70	1:1·90
5. CrW	0·10*M* $CrCl_3·6H_2O$ 0·10*M* $Na_2WO_4·2H_2O$	1:2	6·70	ShGB	ShStGr	ShStGr	0·02	0·02	0·00	1:2·00	1:1·70	1:1·92

CrOH = chromium hydroxide, CrAs = chromium arsenate, CrSb = chromium antimonate, CrMo = chromium molybdate, CrW = chromium tungstate, I.E.C. = ion-exchange capacity, L = light, G = green, Gr = grey, S = sky, Bl = blue, B = black, Sh = shining, St = steel, H.F. = high frequency titration, C.M. = conductimetric titration, C.A. = chemical analysis and X = arsenic, antimony, molybdenum or tungsten.

Ion-exchange studies

Saturation ion-exchange capacity and the pH-titration curves were obtained by the method described earlier.[6,7] The K_d values for inorganic ions have been determined on the hydroxide, antimonate, molybdate and tungstate of chromium(III), and on chromium arsenate without shaking,[7] at pH 3–4. The loading of cations[9] for the system was less than 3% of the experimental ion-exchange capacity. The equation used was

$$K_d = \frac{I - F}{F} \times \frac{50}{0 \cdot 5} \text{ ml/g}$$

where I is the volume of $0 \cdot 002M$ EDTA needed to titrate the original cation solution and F is the volume of $0 \cdot 002M$ EDTA needed for titration after equilibration. The total volume of the equilibrating solution was 50 ml (concentration of each cation solution was $\sim 7 \times 10^{-5}M$) and the amount of the exchanger taken was 0·50 g.

Column preparation

For separation studies a 30 × 0·39 cm bore glass column was used and 1·50 g of chromium molybdate was put in the column with a glass-wool support. The column was washed with demineralized water and the amount of cation added to the column was less than 3% of the experimental ion-exchange capacity of the exchanger. The flow-rate of the effluent was 8–9 drops/min. All the cations other than lead were eluted with $0 \cdot 2M$ ammonium chloride and finally lead was eluted with $1M$ ammonium chloride in $0 \cdot 1M$ nitric acid. The amount of chromium and molybdenum dissolved in $0 \cdot 1M$ nitric acid was found to be 0·00 and $15 \cdot 2 \times 10^{-4}$ g/l. respectively. The cations were determined by EDTA titration and no interference due to the dissolved molybdenum was observed. All other details were similar to those reported earlier.[5–7]

Physical measurements

X-Ray photographs were taken with nickel-filtered Cu$K\alpha$ radiation by the powder method. For infrared studies the KBr disc method was used. For thermoanalytical studies 0·20 g of the exchanger in the hydrogen form was heated at 6°/min. High-frequency and conductimetric titrations of chromium(III) with arsenate, molybdate and tungstate were performed under conditions similar to those used for the synthesis of the respective compounds, *i.e.*, for high-frequency titrations 2 ml of the $0 \cdot 10M$ solution of sodium arsenate, molybdate or tungstate were taken in the cell and a $0 \cdot 10M$ solution of chromic chloride was added from the burette. For the conductimetric titrations 5 ml of the solution were taken in the cell. The reverse titrations were not possible, owing to continuous change in the conductivity of the chromic chloride solution.

Analytical procedure

A 0·20-g portion of the exchanger was oxidized in a porcelain crucible with sodium peroxide and the chromium(III) was titrated volumetrically with ferrous ammonium sulphate.[10] Another 0·20-g portion was dissolved in hydrochloric acid, and arsenic was precipitated as sulphide and determined by Volhard's thiocyanate method.[7] Antimony was also precipitated as the sulphide and determined with potassium iodide.[8] Tungsten and molybdenum were determined as lead tungstate[11] and molybdate[12] after removal of chromium(III) as the hydroxide.

To determine the solubility of the chromium(III) compounds, 0·50 g of the exchanger was shaken for 8 hr with 100 ml of the solution concerned, in a temperature-controlled shaker. The undissolved exchanger was filtered off and in the filtrate chromium was determined spectrophotometrically as dichromate.[13] Arsenic, antimony, molybdenum and tungsten were also determined spectrophotometrically by the molybdenum-blue,[7] Rhodamine B,[8] potassium thiocyanate[12] and sodium thiocyanate[11] methods respectively.

RESULTS

Physical properties

Some of the properties of chromium(III) compounds are recorded in Table I. All the compounds remain as stable gels in water, except chromium arsenate which disperses on shaking. The equilibrium pH of the system consisting of water and the hydroxide, arsenate, antimonate, molybdate and tungstate gels was found to be 3·5, 3·6, 4·6, 3·5 and 3·2 respectively. The gels crack on immersion in water, with slight evolution of heat.

TABLE II.—SOLUBILITY OF HYDROXIDE, ARSENATE, ANTIMONATE, MOLYBDATE AND TUNGSTATE OF CHROMIUM(III), mg/l AT 30 ± 1°C.

	Water		4*M* HCl		4*M* HNO_3	
	Cr	X	Cr	X	Cr	X
CrOH	2·25	—	dc		dc	
CrAs	0·0	5·00	dc		dc	
CrSb	4·25	1·75	dc		21·8	38·0
CrMo	0·0	1·20	dc		dc	
CrW	3·00	0·40	23·0	5·50	11·3	5·0

dc = dissolves completely, X = arsenic, antimony, molybdenum or tungsten.

Chemical properties

The saturation ion-exchange capacity and the change in colour of the exchangers dried at 40, 200 and 500° are recorded in Table I. The ion-exchange capacity of chromium hydroxide at pH 0·75, 7·00 and 12·00 is 1·32 (anion-exchange capacity), 0·00 and 1·64 meq/g (cation-exchange capacity).

Separation studies

The K_d values obtained are recorded in Table III. The ionic radii are those tabulated by Cotton and Wilkinson[14] and reported by Templeton and Dauken.[15] On the

TABLE III.—DISTRIBUTION COEFFICIENTS OF METAL IONS ON HYDROXIDE, ARSENATE, ANTIMONATE, MOLYBDATE AND TUNGSTATE OF CHROMIUM(III) AT 33 ± 1°.

Cations	Ionic radius, *A*°	K_d values, *ml/g*				
		CrOH	CrAs	CrSb	CrMo	CrW
Mg^{2+}	0·65	3	0	$9·0 \times 10^2$	0	0
Ca^{2+}	0·99	0	3	$9·0 \times 10^2$	0	0
Sr^{2+}	1·13	13	3	$4·6 \times 10^3$	6	6
Ba^{2+}	1·35	$1·0 \times 10^2$	37	11×10^3	48	48
Ni^{2+}	0·69	11	5	$5·2 \times 10^3$	0	0
Co^{2+}	0·72	19	23	11×10^3	7	5
Cu^{2+}	0·96	$9·7 \times 10^2$	40	$8·3 \times 10^3$	2	2
Mn^{2+}	0·80	17	36	$3·2 \times 10^2$	56	0
Pb^{2+}	1·21	$3·0 \times 10^3$	$1·8 \times 10^2$	15×10^3	$2·0 \times 10^3$	$2·3 \times 10^2$
VO^{2+}	—	$6·2 \times 10^3$	$4·1 \times 10^2$	$2·9 \times 10^3$	71	50
Zn^{2+}	0·74	27	18	$2·5 \times 10^3$	$1·0 \times 10^2$	13
Cd^{2+}	0·97	$6·6 \times 10^2$	0	$6·0 \times 10^3$	32	14
Hg^{2+}	1·10	$5·6 \times 10^2$	45	$2·0 \times 10^3$	17	20
Al^{3+}	0·50	$2·6 \times 10^2$	29	$2·2 \times 10^3$	29	0
Ga^{3+}	0·62	$1·8 \times 10^3$	$4·3 \times 10^2$	$2·0 \times 10^3$	$5·2 \times 10^2$	2
In^{3+}	0·81	$1·1 \times 10^3$	$5·2 \times 10^2$	$2·4 \times 10^3$	59	9
Y^{3+}	0·93	49	7	$6·6 \times 10^3$	12	7
La^{3+}	1·15	53	16	$6·0 \times 10^3$	22	$1·1 \times 10^2$
Ce^{3+}	1·03	78	33	$7·9 \times 10^3$	19	0
Pr^{3+}	1·01	60	13	$7·5 \times 10^3$	1	1
Nd^{3+}	1·00	66	$1·1 \times 10^2$	$8·2 \times 10^3$	7	25
Sm^{3+}	0·96	71	2	$6·3 \times 10^3$	0	2
Fe^{3+}	0·75	$7·4 \times 10^2$	$3·2 \times 10^2$	$4·1 \times 10^3$	0	0
Th^{4+}	—	$1·9 \times 10^3$	$5·7 \times 10^2$	$4·9 \times 10^3$	100	$4·0 \times 10^2$
ZrO^{2+}	—	$6·1 \times 10^3$	$1·5 \times 10^3$	$6·1 \times 10^3$	$5·2 \times 10^2$	$1·6 \times 10^2$
HfO^{2+}	—	$3·0 \times 10^3$	$3·0 \times 10^3$	$3·0 \times 10^3$	$3·0 \times 10^3$	$3·0 \times 10^3$
Sc^{3+}	0·81	$1·1 \times 10^3$	$1·4 \times 10^2$	$7·1 \times 10^3$	25	44

TABLE IV.—SEPARATION OF Pb^{2+} FROM Ni^{2+}, Co^{2+}, Mn^{2+} AND Cu^{2+} ON CHROMIUM MOLYBDATE COLUMNS.

Mixture separated	Volume of effluent, *ml*	Taken, μg	Found, μg	Error, %
Ni^{2+}	80	220	222	+0·9
Pb^{2+}	130	776	776	0·0
Co^{2+}	100	223	225	+0·9
Pb^{2+}	130	776	791	+1·7
Mn^{2+}	110	207	211	+1·9
Pb^{2+}	120	776	781	+0·7
Cu^{2+}	100	239	236	−1·3
Pb^{2+}	130	776	781	+0·7

basis of the K_d values, Pb^{2+} has been separated[6] from Ni^{2+}, Co^{2+}, Mn^{2+} and Cu^{2+} on chromium molybdate columns (Table IV). In addition to the separation already achieved, some possible separations on the basis of K_d values for chromium(III) compounds are given in Table V.

TABLE V.—POSSIBLE SEPARATIONS OF CHROMIUM(III) COMPOUNDS.

Compound	Possible separations
CrOH	Pb^{2+} from numerous metal ions; Al^{3+} from Ga^{3+} and In^{3+}; La^{3+} from Sc^{3+} and Th^{4+}; and Sc^{3+} from Y^{3+} and Ca^{2+}.
CrAs	Mg^{2+} from Al^{3+} and Sc^{3+}; HfO^{2+} from Th^{4+}; and Sm^{3+} from Nd^{3+}.
CrSb	Mg^{2+} from Ba^{2+}, Cu^{2+}; Ca^{2+} from Ba^{2+}; Mn^{2+} from Co^{2+}, Ni^{2+}, Cu^{2+}, Al^{3+}, VO^{2+} and Fe^{3+}; and La^{3+} from Ca^{2+}.
CrMo	Ba^{2+} from Mg^{2+} and Ca^{2+}; Ga^{3+} from In^{3+}, Al^{3+} and Fe^{3+}; and HfO^{2+} from ZrO^{2+}.
CrW	HfO^{2+} from numerous metal ions; La^{3+} from Ce^{3+}, Pr^{3+} and Sm^{3+}; and Pb^{2+} from Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+}.

Physical studies

X-Ray powder photographs show that all five compounds in the hydrogen form and dried at 40° are amorphous.

Infrared spectra of the five compounds dried at different temperatures are similar and resemble those reported for antimonic acid and sodium antimonate.[1] Therefore a similar band assignment may be given as follows. The bands with maxima at about 3300, 1380 and 1610 cm^{-1} are characteristic of the stretching vibration of interstitial water and OH groups [$\nu_1(H_2O \text{ or } OH)$], the M—OH deformation vibration [$\delta_2(OH)$] and the deformation vibration of interstitial water [$\delta_1(H_2O)$] respectively. The band with maxima at about 600–480 cm^{-1} is due to the stretching vibration of M—O [$\nu_2(Cr—O)$] and the deformation vibrations of anions [$\delta_3(AsO_4)$].

The thermoanalysis results are shown in Figs. 1 and 2.

DISCUSSION

All the five salts of chromium(III), reported here, were first prepared under varying conditions. The conditions of preparation finally chosen were those which appeared to give reproducible and fairly stable products. These conditions were adhered to in all preparations to facilitate comparison. The results of chemical composition of arsenate, molybdate and tungstate of chromium(III) obtained by electrometric titrations are in good agreement with those obtained by chemical analysis (Table I). Chromium

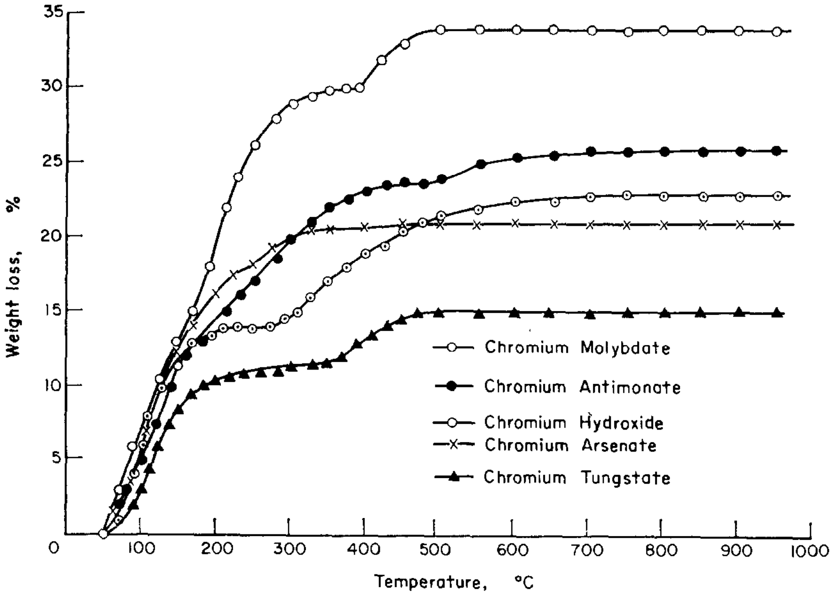


FIG. 1.—TGA graphs of chromium(III) compounds.

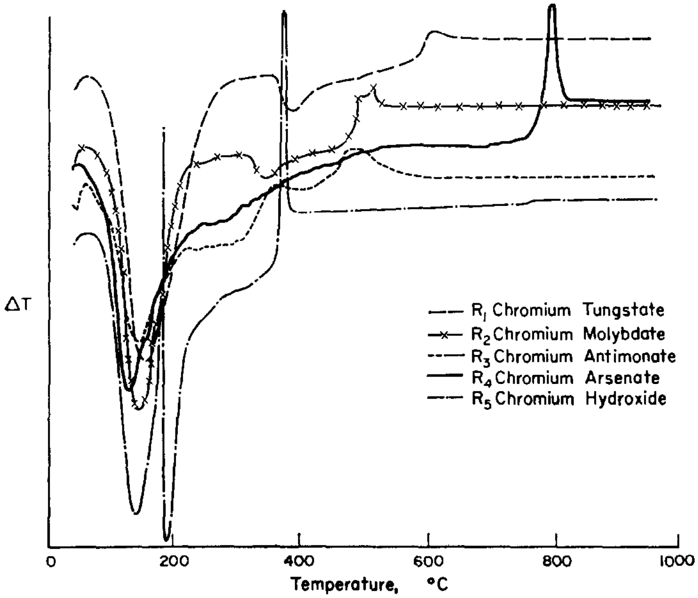
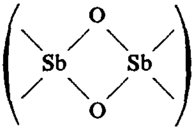


FIG. 2.—DTA graphs of chromium(III) compounds.

antimonate has a composition different from that of the other compounds studied. The great tendency of antimony pentachloride to hydrolyse even in dilute mineral acids, as distinct from arsenate, molybdate and tungstate, is responsible for this deviation. Nitrogen was not detected in the hydroxide and antimonate of chromium(III), and there is therefore no possibility of either NH_3 or NH_4^+ being present in these compounds.

The infrared spectra show that the band at 1610 cm^{-1} is absent in the compounds dried at 200° except in the case of chromium antimonate in which it is absent if the compound is heated to 500°. The intensity of the bands located at 3300 and 1380 cm^{-1} is also diminished as the drying temperature increases. At 500° the bands observed correspond to the respective oxides. The sequence for the thermal stability of the exchangers on the basis of infrared studies is CrSb > CrAs > CrOH > CrMO > CrW. It is also clear from the infrared spectra that all the compounds under study contain free water molecules as well as OH groups. The hydrogen ions attached in the form of OH groups are responsible for the ion-exchange capacity. These chromium(III) compounds are probably formed as a result of condensation of chromium hydroxide with the hydrated oxides of arsenic, antimony, molybdenum and tungsten. The monofunctional behaviour and cation-exchange capacity data (Table I) support these conclusions. Thermoanalytical results (Figs. 1 and 2) show that the weight loss % is in the order CrOH > CrSb > CrMo > CrAs > CrW, but because the formula weights differ so much, this is not a guide to the degree of hydration, which is in the order CrSb > CrW > CrMo > CrAs > CrOH. The TGA and DTA curves are similar to those reported for zirconium phosphate.[16] The exothermic peak at 380° in the DTA curve of chromium hydroxide, not found for other compounds, may be due to the conversion of chromium hydroxide into the oxide. At above 500° the weight of all the compounds is almost constant. Therefore the endothermic peaks at 170–190° seem to be due to the loss of either free water or water formed by the condensation of OH groups, and the exothermic peaks at higher temperatures are due to the formation of the corresponding oxides. The gradual change in the colour and the ion-exchange capacity of the compounds with increase in drying temperature (Table I) confirm these conclusions.

On the basis of these observations and the reported[17] species



the following tentative structure, similar to that of titanium antimonate[3] and hydrated chromium sulphate,[18] may be postulated for the chromium(III) compounds. Consider the case of chromium antimonate.

The Cr: Sb ratio by chemical analysis is 1:2·95. On heating, the oxides are produced, which should be in the same mole ratio. Allowing for experimental error, this may be rounded off to a 1:3 ratio. Therefore the empirical formula weight for $Cr_2O_3 \cdot 3Sb_2O_5$ is approximately 1122. The total weight loss on heating is 26%, so if n is the number of moles of water per mole of "mixed oxide",

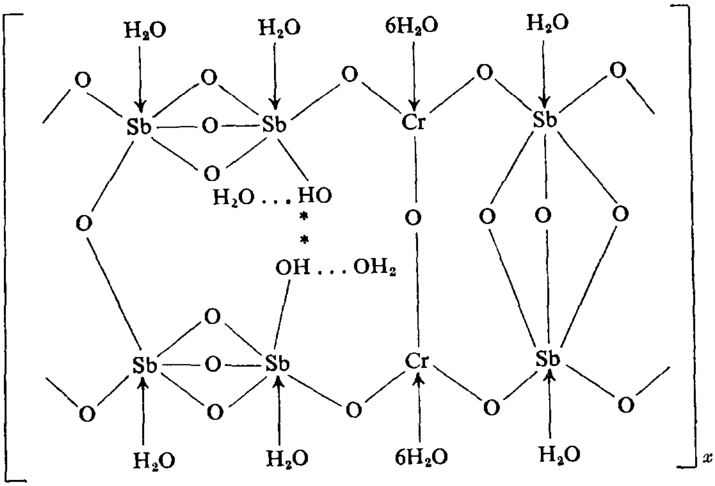
$$1800n/(1122 + 18n) = 26 \text{ and } n = 21{\cdot}9.$$

Again allowing for error in the TG work, we can write the formula as

$$Cr_2O_3{\cdot}3Sb_2O_5{\cdot}22H_2O,$$

formula weight 1442. The cation-exchange capacity on the basis of two protons per formula weight is 2000/1442 = 1·39 meq/g.

Therefore the structure of chromium antimonate may be written as:



where the protons marked with an asterisk are those considered responsible for the ion-exchange.

For the other compounds we have $Cr_2O_3{\cdot}4H_2O$, $Cr_2O_3{\cdot}2As_2O_5{\cdot}9H_2O$, $Cr_2O_3{\cdot}4MoO_3{\cdot}12H_2O$ and $Cr_2O_3{\cdot}4WO_3{\cdot}15H_2O$, which may be written as $Cr(OH)_3{\cdot}H_2O$, $Cr_2O_3(\overset{**}{H}_3AsO_4)_4{\cdot}3H_2O$, $Cr_2O_3(\overset{*}{H}_2MoO_4)_4{\cdot}8H_2O$ and $Cr_2O_3(\overset{*}{H}_2WO_4)_4{\cdot}11H_2O$. The hydroxide groups attached to chromium do not appear to have exchangeable protons whereas those attached to arsenic, antimony, molybdenum or tungsten do. The ion-exchange capacity calculated as above is always greater than the experimental ion-exchange capacity given in Table I. The amorphous nature of the compounds, *i.e.*, non-availability of all the exchange sites at neutral pH, may be responsible for this deviation.

The important sequences for the various chromium(III), tin(IV) and titanium(IV) compounds are given in Table VI. It is obvious from Table VI that the properties of the exchangers depend upon the composition of the material, *i.e.*, the tungstate is the most stable in nitric acid, the antimonate has the highest thermal stability and ion uptake, while the arsenate shows the greatest ion-exchange capacity. These facts support our earlier work on exchangers containing tin or titanium instead of chromium(III) (Table VI).

Like other hydroxides,[21,22] chromium hydroxide strongly adsorbs those cations which are prone to hydrolysis, *e.g.*, VO^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}, Th^{4+}, ZrO^{2+}, HfO^{2+} and Sc^{3+} and it shows a lower uptake for bivalent cations at neutral pH (Table III). The molybdate and tungstate of chromium(III) are selective as they have high K_d values for certain metal ions only. The corresponding arsenate and antimonate show high uptake for all cations (Table III). Therefore the insoluble chromium compounds may be used to achieve separations and to soften water, though

TABLE VI.—COMPARISON OF Cr(III), Sn(IV) AND Ti(IV) ION-EXCHANGERS.

Property	Sequence of chromium(III) exchangers	Sequence of tin(IV) exchangers	Sequence of titanium(IV) exchangers
Stability in water	CrMo > CrW > CrOH > CrAs > CrSb	SnSb > SnW > SnAs > SnMo	TiW ~ TiSb > TiAs > TiMo
Stability in HNO_3	CrW > CrSb > CrAs ~ CrMo ~ CrOH	SnW > SnSb > SnAs > SnMo	TiW > TiSb > TiMo > TiAs
Ion uptake	CrSb > CrOH > CrAs > CrMo > CrW	SnSb > SnMo > SnW > SnAs	TiSb > TiW > TiAs > TiMo
Thermal stability on the basis of ion-exchange capacity	CrSb > CrAs > CrW > CrMo > CrOH	SnAs > SnSb > SnW > SnMo	TiAs > TiW > TiMo
Cation-exchange capacity at neutral pH	CrAs > CrSb ~ CrW > CrMo > CrOH	SnAs > SnMo > SnSb > SnW	TiAs > TiMo > TiW > TiSb

SnSb = stannic antimonate (unpublished work), SnAs = stannic arsenate,[6,7] SnW = stannic tungstate,[19] SnMo = stannic molybdate,[8] TiSb = titanium antimonate,[8] TiAs = titanium arsenate,[20] TiW = titanium tungstate,[11] and TiMo = titanium molybdate.[12]

toxicity studies would be necessary for the latter application. Their chief advantage is that they are inexpensive and are easily prepared. Their disadvantage is that they are not very stable in acids. It is unfortunate that Szirtes *et al.*[4] did not report the chemical stability of their chromium(III) phosphate. Our results suggest that it should not be very stable.

Acknowledgement—We thank Dr. S. M. F. Rahman for research facilities and Dr. B. Rama Rao for X-ray facilities. Financial assistance (to R. K.) and to (H. S. R.) by the UGC (India) and CSIR (India) is gratefully acknowledged.

Zusammenfassung—Fünf wasserunlösliche Chrom(III)-Verbindungen wurden durch Mischen von 0,10*M* Chrom(III)-chloridlösungen und Lösungen der entsprechenden Natriumsalze im Volumenverhältnis 1:2 bei pH 6-7 hergestellt. Ihre Ionenaustausch-Eigenschaften wurden verglichen. Das Wolframat besitzt die größte chemische Stabilität, das Arsenat die höchste Ionenaustauschkapazität. Chrom(III)-molybdat Säulen wurden zur Abtrennung von Pb^{2+} von zahlreichen Metallionen verwendet.

Résumé—On a synthétisé cinq composés insolubles dans l'eau du chrome(III) en mélangeant des solutions 0·10*M* de chlorure chromique et des sels de sodium appropriés dans le rapport de volumes 1:2, à pH 6–7. On a comparé leurs caractéristiques d'échange d'ions. Le tungstate a la stabilité chimique la plus élevée et l'arséniate à la plus forte capacité d'échange d'ions. On a utilisé des colonnes de molybdate de chrome(III) pour séparer Pb^{2+} de nombreux ions métalliques.

REFERENCES

1. M. Abe and T. Ito, *Bull. Chem. Soc. Japan*, 1963, **41**, 2366.
2. J. D. Donaldson and M. J. Fuller, *J. Inorg. Nucl. Chem.*, 1970, **22**, 1703.
3. M. Qureshi and V. Kumar, *J. Chem. Soc.*(*A*), 1970, 1488.
4. L. Szirtes, L. Zsinka, K. B. Zaborenko and B. Z. Iofa, *Acta Chem. Acad. Sci. Hung.*, 1967, **54**, 215.
5. M. Qureshi, H. S. Rathore and R. Kumar, *J. Chromatog.*, 1971, **54**, 269.
6. *Idem*, *J. Chem. Soc.*(*A*), 1970, 1986.
7. M. Qureshi, R. Kumar and H. S. Rathore, *ibid.*, 1970, 272.
8. M. Qireshi, K. Husain and J. P. Gupta, *ibid.*, 1971, 29.
9. H. Hamaguechi, R. Kuode, K. Aoki, R. Sugista and N. Onuma, *Talanta*, 1963, **10**, 153.
10. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, p. 524. Wiley, New York, 1953.
11. M. Qureshi and J. P. Gupta, *J. Chem. Soc.*(*A*), 1970, 2620.
12. M. Qureshi and H. S. Rathore, *ibid.*, 1969, 2515.
13. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, p. 390. Interscience, New York, 1959.
14. F. A. Cotton and G. Wilkinson, *Advances in Inorganic Chemistry*, p. 45. Interscience, New York, 1964.
15. D. M. Templeton and C. H. Dauken, *J. Am. Chem. Soc.*, 1954, **76**, 5276.
16. A. Clearfield and A. S. Medinae, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2775.
17. I. H. Baetsle and D. Huys, *ibid.*, 1968, **30**, 639.
18. H. Remy, *Treatise on Inorganic Chemistry*, pp. 119–144. Elsevier, New York, 1956.
19. M. Qureshi and K. G. Varshney, *J. Inorg. Nucl. Chem.*, 1968, **30**, 3081.
20. M. Qureshi and S. A. Nabi, *ibid.*, 1970, **32**, 2059.
21. C. B. Amphlett, *Inorganic Ion Exchangers*, p. 91. Elsevier, New York, 1964.
22. C. Hietner-Wirguin and A. Albu-Yaron, *J. Inorg. Nucl. Chem.*, 1966, **28**, 2379.

Talanta, 1972, Vol. 19, pp. 1387 to 1419. Pergamon Press. Printed in Northern Ireland

INVESTIGATIONS OF DIOXIMES AND THEIR METAL COMPLEXES

A SURVEY OF THE LITERATURE SINCE 1963

BIRGITTA EGNEUS
Department of Analytical Chemistry, University of Gothenburg,
Fack S-402 20 Göteborg, Sweden

(*Received* 28 *February* 1972. *Accepted* 26 *March* 1972)

Summary—A review is given of the chemistry and analytical applications of dioxime complexes from metals.

VICINAL α-dioximes have been used as analytical reagents for transition metals, especially nickel and palladium, since Tschugaeff[1] in the beginning of the 20th century discovered and outlined the selective properties of the dioximes. The most studied and used dioxime is dimethylglyoxime, which with nickel forms a characteristic scarlet precipitate, slightly soluble in water. Other widely used dioximes are α-furildioxime, where $R = R' = C_4H_3O$ (see Fig. 1), and the ring-stabilized 1,2-cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime (nioxime and heptoxime respectively), where RCCR′ (Fig. 1) is cyclohexane and cycloheptane respectively. These reagents are as selective as dimethylglyoxime and have the advantage of being more soluble in water.[2]

Many investigations have been carried out to study the complexation properties of dioximes. Most transition metals form some kind of stable complex with these compounds. Usually the metal ion is co-ordinated to the functional group C(NOH)—C(NOH) of two dioxime molecules, as shown in Fig. 1, because the formation of four chelate rings will increase the stability of the complex.

With the aim of finding useful analytical reagents, the effect on the precipitation of several transition metals when the substituents in a dioxime are changed has been studied.[3,4] Dioximes prepared from large-ring diketones have thus been reported which precipitate bismuth, nickel and palladium.[5] For some dioximes used as analytical reagents, an attempt has been made to find a correlation between the electronic structure parameters (net π-electron charge on the oxygen atoms) and some thermodynamic quantities.[6] The results are, however, too meagre to allow a theoretical selection of dioximes for the determination of a certain metal.

Extensive reviews have previously been written by Babko,[7] Banks,[8–10] Dyrssen,[11] and Burger.[12] The present review deals mainly with the investigations related to the solution chemistry of the most common dioximes and their metal complexes that have been published and recorded in abstracts from January 1963 up to October 1971. It therefore constitutes a supplement to the review by Dyrssen.[11] Analytical procedures are summarized in condensed form only.

SEPARATION AND IDENTIFICATION OF DIOXIME ISOMERS

Orientation of the hydroxyl groups

Besides *cis* and *trans* configurations (see next section) the hydroxyl groups can be oriented in three ways relative to each other, Fig. 2*a*, *c*, *d*. The anti isomer (α-form)

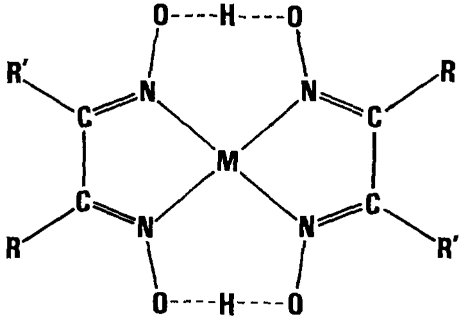
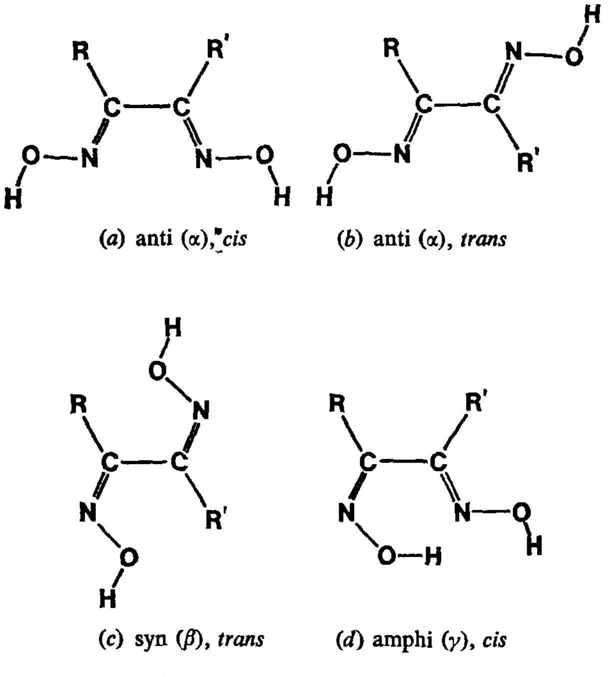


Fig. 1.—The structure of metal dioxides, $M(HA)_2$. R and R′ denote H, aliphatic or aromatic radicals.



(a) anti (α), cis (b) anti (α), trans

(c) syn (β), trans (d) amphi (γ), cis

Fig. 2.—The isomers of dioximes, H_2A.

is known to form complexes with metal to ligand ratio 1:2, whereas the amphi isomer (γ-form) forms 1:1 complexes. The syn isomer (β-form), for steric reasons forms no complexes. The synthesis of an aromatic α-dioxime usually yields β- and γ-isomers as by-products, but there is little evidence of the formation of β- and γ-isomers in the preparation of aliphatic and alicyclic dioximes.[13] The mixed aliphatic-aromatic dioximes and the chlorodioximes are, however, known to exist as both anti and amphi isomers, see, *e.g.*, Toul *et al.*[14] and Ungnade *et al.*[15] The isomers are usually identified by chromatographic or spectroscopic methods, which have replaced such chemical methods as colour of solid metal derivates and isomerization with acids and bases. Thin-layer chromatography (TLC) has successfully been used by Toul *et al.*[14] to separate and identify benzilmonoxime, benzildioxime, furilmonoxime, furildioxime and their isomers, and dimethylmonoxime in dimethylglyoxime. Fractional recrystallization has been utilized by Burakevich *et al.*[16] to isolate three isomers of phenylglyoxime. The anti-, amphi- or syn-structures were identified by TLC and reactions with nickel(II) ions. Isomers have also been identified by using the ultraviolet and infrared spectra of the dioximes[15] or the ultraviolet and visible spectra of metal derivatives in solution.[17–19]

Nuclear magnetic resonance (nmr) spectroscopy seems to be a useful tool for identifying the isomers of a dioxime. Different chemical shifts, depending on the orientation of the oxime groups, are obtained for the protons in substituents adjacent to the oxime groups and for the hydroxyl protons. As the chemical shift of the hydroxyl proton is concentration-dependent, the chemical shifts of the protons in the substituents have been used in developing criteria for the different isomers in carbon tetrachloride and deuterated chloroform media. A shift independent of the concentration is, however, obtained in dimethylsulphoxide (DMSO), if the solution contains less than 5 mole $\%_0$ of the dioxime.[20] Guetté *et al.*[21] have calculated theoretically the chemical shifts of the hydroxyl protons of some dioximes and ketone oximes in DMSO in relation to the polarities and the configurations of the substituents of the rest of the molecule. The calculations are in fairly good agreement with experimentally obtained data. Tanaka *et al.*[22] have reported an analytical application of nmr, using the chemical shifts assumed to be due to the different isomers of benzil- and furildioxime. It was also shown that commercially available furildioxime may be a mixture of α- and γ-furildioximes.

Cis *and* trans *isomerism of the α-oxime groups*

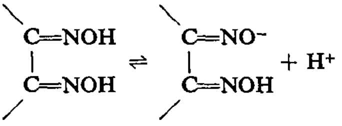
The oxime groups can be *cis* or *trans* to each other, Fig. 2*a*, *b*. Crystalline glyoxime[23] and dimethylglyoxime[24,25] have been shown to have the *trans* configuration. The configuration in the metal chelate must, however, be *cis*. It has been discussed whether the configuration of aliphatic anti-dioximes is *cis* or *trans* in solution.[26] From an infrared investigation of glyoxime it has been concluded that this compound must have a *trans* configuration in solution.[27] Theoretical calculations on the π-electron systems of the *cis* and *trans* configurations of dimethylglyoxime have been made by Roos,[28] and Bossa and Morpurgo.[29] The absorption bands in the ultraviolet region and the oscillator strengths have been calculated for each configuration and compared with experimental data. The investigators have used different parameters for their calculations. The results by Roos[28] indicate that dimethylglyoxime has a *cis* configuration, whereas Bossa and Morpurgo[29] claim that the configuration must be *trans*. The *trans* configuration is supported by an extensive study of dipole measurements of dimethylglyoxime and other dioximes in dioxan.[26] The ultraviolet spectra of ethylmethylglyoxime, and its singly and doubly charged anions have been determined by Egneus.[30] These results fit with the molecular calculation on the *cis* configuration by Roos.[28] The solvent effect may, however, be important.

Cyclic dioximes cannot have a *trans* configuration, as the oxime groups are fixed by the aliphatic ring in the *cis* position. Measurements of the maximum molar absorptivity in the ultraviolet region have shown that cyclic dioximes have a lower value than other, non-cyclic, dioximes.[31] The maximum molar absorptivities of the complexes between a metal and various dioximes are, however, nearly the same,[11] irrespective of the configuration of the dioxime in its uncomplexed form.

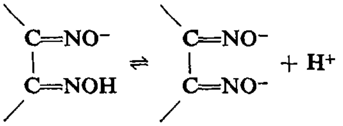
ACID AND BASIC BEHAVIOUR OF DIOXIMES; DECOMPOSITION IN ACID MEDIUM

Spectrophotometric investigations

In alkaline solution the dioxime splits off one or two protons according to equations (1) and (2).



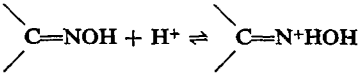
(1)



(2)

The dissociation constant for equation (1) is generally about $10^{-10.5}$ and for equation (2) about 10^{-12} (see ref. 2 and Table II).

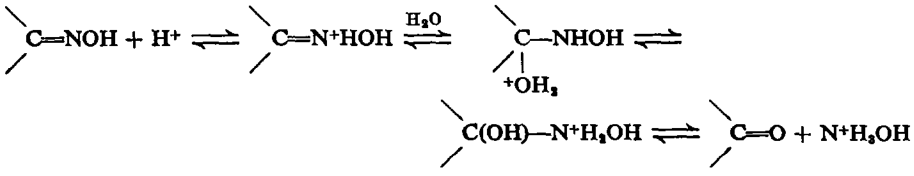
The nitrogen atom of the oxime group has weak basic properties, and a protonation according to equation (3) takes place in acid medium.



(3)

The protonation causes a bathochromic shift of about 20–30 nm from the maximum absorption wavelength of the neutral dioxime, with little or no change of the molar absorptivity.[31] The protonation constant can thus be determined spectrophotometrically. The protonation constant for dimethylglyoxime was found by Ellefsen and Gordon[32] to be 0·115 in hydrochloric acid at 25°. Shlenskaya *et al.*[31] obtained a value of 0·172 in perchloric acid at 25°. The decomposition that takes place in acid solution was considered in both works. The investigation by Shlenskaya *et al.*[31] indicates that alicyclic dioximes, *e.g.*, nioxime, have higher protonation constants than aromatic dioximes, *e.g.*, α-benzildioxime.

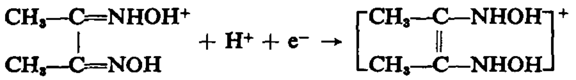
Alybina and Peshkova[33] have spectrophotometrically investigated the decomposition of dioximes in acid media with respect to time and concentration of hydrogen ions. The stability decreases in the following order: α-benzildioxime > dimethylglyoxime > heptoxime > nioxime. It seems as if a dioxime with lower protonation constant is less readily decomposed than a dioxime with a higher protonation constant. This implies that the first step of the decomposition is a protonation. The ultraviolet spectrum of nioxime in 5*M* hydrochloric acid measured after 5 hr shows the same features as the spectrum of the corresponding diketone. The decomposition may thus be a hydrolysis of the dioxime according to the reactions in equation (4).



(4)

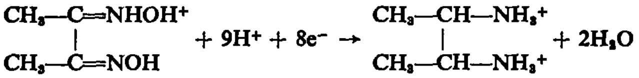
Polarographic investigations

The polarographic behaviour of dimethylglyoxime in acid solution has been studied by Spritzer and Meites.[34] A single well-defined wave is obtained at pH values below 3·5. A new wave appears at a more negative potential at pH values between 3·5 and 5·5. At pH values above 7 only an ill-defined wave at a very negative potential is obtained. The reduction product at pH values below 3·5 has been identified as 2,3-diaminobutane. The decomposition involves two protonation steps, but only one of the protonated intermediates is reduced. The rate-determining step is supposed to be



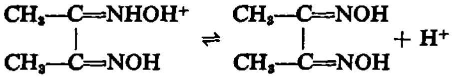
$$\begin{array}{l}CH_3—C{=}NHOH^+\\ \quad|\\ CH_3—C{=}NOH\end{array} + H^+ + e^- \rightarrow \left[\begin{array}{l}CH_3—C—NHOH\\ \quad\;\|\\ CH_3—C—NHOH\end{array}\right]^+ \tag{5}$$

The overall reduction is suggested to proceed according to

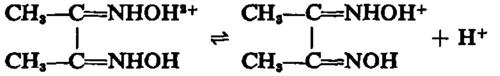


$$\begin{array}{l}CH_3—C{=}NHOH^+\\ \quad|\\ CH_3—C{=}NOH\end{array} + 9H^+ + 8e^- \rightarrow \begin{array}{l}CH_3—CH—NH_3^+\\ \quad|\\ CH_3—CH—NH_3^+\end{array} + 2H_2O \tag{6}$$

Burger *et al.*[35] have determined the dissociation constants for the two protonated species, equations (7) and (8).



$$\begin{array}{l}CH_3—C{=}NHOH^+\\ \quad|\\ CH_3—C{=}NOH\end{array} \rightleftharpoons \begin{array}{l}CH_3—C{=}NOH\\ \quad|\\ CH_3—C{=}NOH\end{array} + H^+ \tag{7}$$



$$\begin{array}{l}CH_3—C{=}NHOH^{2+}\\ \quad|\\ CH_3—C{=}NHOH\end{array} \rightleftharpoons \begin{array}{l}CH_3—C{=}NHOH^+\\ \quad|\\ CH_3—C{=}NOH\end{array} + H^+ \tag{8}$$

The overall reaction in equation (6) was found to take place. However, the polarographic data obtained can only be explained by assuming that both the protonated species are reduced. The values of the dissociation constants are $10^{-3\cdot00}$ and $10^{-3\cdot27}$ respectively. The value obtained for equation (7) is much lower than that determined spectrophotometrically.[31,32]

The reduction of dimethylglyoxime with stannous chloride in acid medium with molybdate as catalyst, has been proposed as proceeding through the formation of diacetyl.[36] The final reduction products have been identified as ammonia and acetoin [$CH_3CH(OH)COCH_3$].

The decomposition of dimethylglyoxime in hydrochloric acid has been studied by polarographic measurements.[34,36] The decrease of the concentration of dimethylglyoxime is proportional to the concentrations of unreacted dioxime and hydrogen ions.[34] The value of the decomposition rate constant is $1\cdot13 \times 10^{-3}$ l.mole^{-1}.sec^{-1} in $0\cdot1M$ sodium chloride–hydrochloric acid medium containing 15% ethanol. Different decomposition products have been proposed; 2,3-dinitrobutane was identified from its infrared spectrum,[34] and polarographic data indicated hydroxylamine and diacetylmonoxime.[36] No diacetyl was found in the reaction mixture.[34,36]

It should be observed that usually the protonation and the decomposition of dioximes need not be considered in the formation of metal complexes, unless the hydrogen ion concentration is high and the equilibrium time is long. Practically, it is only the formation of palladium complexes that can be affected.

The polarographic behaviour of dimethylglyoxime in alkaline medium has been suggested to be due to a four-electron process.[37] A dihydroxylamine might be the reduction product.

The polarographic behaviour of α-furildioxime has been studied in detail by Gelb and Meites.[38] The reduction proceeds in two distinct steps, both consisting of several stages. The first step involves six electrons. The product obtained will undergo transformation at a rate that depends on the hydrogen ion concentration. Further electrons may then be accepted. The final reaction product will depend on the hydrogen ion concentration at the different stages of the reaction. Under most conditions eight electrons are consumed and the reaction product has been identified as 1,2-bis-(2-furil)ethylenediamine (*cf.* dimethylglyoxime).

STRUCTURE OF METAL COMPLEXES

X-ray analysis of simple complexes

Many 1:2 complexes of bivalent transition metals with α-dioximes have been isolated. The crystal structure has been determined by X-ray spectrometry for a number of them. A collection of crystal data is given in the review by Dyrssen.[11] The characteristic feature of a 1:2 dioxime complex is the co-ordination of the four nitrogen atoms to the metal atom (central atom), Fig. 1. The nitrogen–metal bonds are usually in nearly the same plane and are almost of the same length (1·85–1·96 Å). The distances between the neighbouring oxygen atoms (hydrogen bonds) in a molecule are short; the measured values[11] are between 2·33 and 3·03 Å. The intramolecular hydrogen bonds between these oxygen atoms give an increased stability to the complex through the ring formation (see Fig. 1). The positions of the hydrogen atoms have not been definitely located, and it is still unknown whether the hydrogen bonds in dioxime complexes are linear or not. The long hydrogen bond in platinum(II) dimethylglyoximate (3·03 Å) has been queried by Schlemper,[39] who has found shorter oxygen–oxygen distances in similar nickel and platinum compounds.

A refinement of the structure of copper bisdimethylglyoximate has been made by Vaciago and Zambonelli,[40] using three-dimensional data obtained at room temperature. The crystal data differ little from those obtained earlier by Frasson *et al.*[41] who used low temperature and two-dimensional data. It could be argued[40] that cyclic delocalization of the electrons in the carbon–nitrogen bond might take place. Several resonance forms would then contribute to the stability. From the lengths of the copper–nitrogen bond it has, however, been concluded that no delocalization is likely to occur.

The crystal structure of copper dimethylglyoximate dichloride has been determined by Svedung.[42] The copper atom is co-ordinated by two nitrogen atoms within a molecule and the fifth co-ordination is offered by a chlorine atom of an adjacent molecule. The dimers thus formed are held together by two copper–chlorine–copper bridges. The triclinic structure is built up by chains of dimers, which are held together by intermolecular hydrogen bonds between pairs of oxygen atoms.

Many of the most studied nickel and palladium complexes[43] are isomorphous with nickel dimethylglyoximate. In these complexes the metal atoms are stacked above each other. Metal–metal chains, which were first proposed for nickel dimethylglyoximate,[44] have been proposed as a common property of these nickel and palladium dioximates. However, X-ray investigations show that nickel,[45,46] palladium[47] and platinum[48] glyoximates are not isomorphous with nickel dimethylglyoximate. None of these complexes has any appreciable metal–metal bonding. Nickel ethylmethylglyoximate, which exists in the two modifications α- and β- (according to the nomenclature of Anex and Krist[49]), in its β-form is isomorphous with nickel dimethylglyoximate. The α-form is isomorphous with nickel glyoximate. The nickel–nickel distances are 4·74 and 4·196 Å respectively[45,50] compared to 3·4 and 3·25 Å for β-nickel ethylmethylglyoximate[51] and nickel dimethylglyoximate.[44] No metal–metal interaction is thus possible in α-nickel ethylmethylglyoximate. A method of calculating the densest molecular arrangements of layers in crystals has been developed by Zorkii *et al.*[52] The predicted packing for nickel dimethylglyoximate is very close to that found experimentally, though it does not attain the highest possible density.

X-ray analysis of binary complexes

The structures of binary (mixed) dimethylglyoxime complexes containing two of the metals nickel, palladium and platinum, have been determined by X-ray diffraction by Lindoy *et al.*[53] The difference between the cell constants of the simple nickel, palladium and platinum dimethylglyoximates is small.[53] The binary complexes are isomorphous with the simple ones and have the metal–metal distances 3·23–3·25 ± 0·02 Å. The X-ray data have shown that, *e.g.*, two nickel and two palladium atoms in the unit cell occupy four equivalent crystallographic positions. The mixed complexes can therefore be supposed to built up in such a way that the metal atoms alternate in the metal chain extending through the crystal lattice. A disordered stacking sequence is, however, necessary to get a structure isomorphous with the simple complexes.[53] The close relationship between the structures of different bivalent transition metals explains the possibility of interfering co-precipitation of nickel, palladium and platinum dimethylglyoximates with each other in analysis.[54,55]

Spectrophotometric investigations of crystals in the ultraviolet–visible wavelength region

Several spectral investigations have been made of single crystals of some metal dioximates, particularly nickel dimethylglyoximate. Both polarized and unpolarized light have been used to make clear the interaction between the central atoms in the crystals. It was first reported by Yamada and Tsuchida[56] that crystals of nickel and palladium dimethylglyoximate have an anomalous dichroism and show characteristic absorption bands around 500 nm that are not present in the spectra of the corresponding solutions. These facts have been taken as support for the weak metal–metal interaction first proposed by Godycki and Rundle.[44] Banks and Barnum[57] have supported the metal–metal bond theory from their investigation of the absorption spectra of several solid nickel and palladium dioximates supposed to have metal–metal interactions. The characteristic absorption band for a metal complex in colloidal solution will shift to a longer wavelength when the metal–metal distance increases.[57] The position of the band will also depend on the central metal ion and the crystal structure. The absorption band of single crystals of nickel dioximates, in plane polarized light at about 500 nm, shows "abnormal" dichroism when the nickel–nickel distance is short. Normal dichroism occurs when the nickel–nickel distance is long.[57]

A possibility of verifying or disproving the intermetallic bonding theory is offered by studying the two modifications of solid nickel ethylmethylglyoximate (*cf.* above). Anex and Krist[49] have made an extensive investigation on the spectra of single crystals, solid films and solutions of α- and β-nickel ethylmethylglyoximate, nickel dimethylglyoximate and nickel heptoximate. From their results they have concluded that the characteristic band is of an intramolecular nature.

Another explanation, given by Ohashi *et al.*[58] is that the odd absorption band of the solid phase is due to a transition within the nickel ion. The intensity of the band is probably increased by an interatomic charge-transfer excitation in the crystal. Ohashi *et al.*[58] calculated the ground state stabilization energy to be 5 kcal/mole for nickel dimethylglyoximate. This is considerably less than the value of 10 kcal/mole for the strength of the nickel–nickel bond calculated from solubility data by Banks and Anderson.[59] A molecular orbital study by Ingraham[60] on nickel dimethylglyoximate has shown no strong nickel-nickel interaction. However, in general, the molecular orbital calculations suffer from the disadvantage of dependence on the parameters used. Thus the quantitative aspects of these calculations are somewhat uncertain.

Basu *et al.*[54] have investigated the temperature dependence of the absorption spectra of the solid, mixed, binary complexes of copper, nickel, palladium, and platinum with dimethylglyoxime. The absolute intensity is measured. No evidence for metal–metal bonds is obtained. On the basis of these experiments it is suggested that dioxime-complexes with the metal atoms stacked on top of each other (dimethylglyoximates of nickel, palladium and platinum) owe their crystal structure more to a favourable packing than to intermolecular bonds.

From a molecular orbital treatment of the absorption bands of copper bisdimethylglyoximate Roos[61] has given a theoretical explanation of the dimerization of the complex in the solid state. A covalent bond can be formed between a filled metal orbital of a molecule and an empty orbital of another molecule. The dimer should be further stabilized through the electrostatic interaction between a negatively charged oxygen atom and a positively charged copper atom.

Spectrophotometric investigations of metal complexes in solution in the ultraviolet–visible wavelength region

Much information about the bonds and the co-ordinations within a complex dissolved in various solvents is given by the ultraviolet and visible absorption spectra. Satisfactory assignments of the bands require, however, theoretical calculations combined with experimental data. Copper(II), cobalt(II) and iron(II) dioximates, which have preferably octahedral or distorted octahedral or square pyramidal configuration, have been investigated to study the effects on the ultraviolet–visible absorption spectrum by adduct formation, replacement of ligands, substitutions in the ligands, solvent interactions and changes in the bond strength, *etc.* Nickel(II), palladium(II) and platinum(II) dioximates have a square planar symmetry and a small tendency to be co-ordinated with axial unidentate ligands, in contrast to the cobalt(II), copper(II) and iron(II) complexes.

The ultraviolet–visible absorption spectra of copper- and nickel dimethylglyoximates and nickel ethylmethylglyoximate have been recorded by Caton and Banks.[62] Copper dimethylglyoximate exhibits significant solvent shifts, which have been assigned to changes in the nature of the copper–nitrogen bonds, due to an interaction between the complex and the solvents. No shift is observed for the nickel complexes. This partly reflects the inability of nickel dioximates to form adducts. A theoretical investigation of the normal (isolated molecule) and the excited states of copper dimethylglyoximate and its adducts with water and amines has been made by Roos.[61] The experimental data obtained by Dyrssen and Petković[63] were used. The results[61] show that a configuration interaction takes place between the ligand field and the charge-transfer transitions in copper dimethylglyoximate. This fact should be considered when interpreting spectral data from metal complexes with strong π-bondings. From the best agreement between theoretical data, calculated for a five- or six-co-ordinated copper ion, and experimental data,[63] the adducts with amines (B) and water are found to be $Cu(HA)_2B$ and $Cu(HA)_2(H_2O)_2$ respectively.

Iron(II) dioximates with the composition $Fe(HA)_2(pyridine)_2$ have a strong absorption band between 510 and 570 nm, which has been assigned to the metal → dioxime charge-transfer.[64–66] The position of this absorption band is correlated[64] to the C=N stretching band at 1500 cm^{-1} and the vibration band for Fe–N in the region 650–500 cm^{-1}. The charge-transfer band and the C=N stretching band of these complexes shift towards longer wavelengths in the order dimethylglyoxime < nioxime < α-benzildioxime < α-furildioxime, while the Fe–N vibration band will shift towards shorter wavelengths.[64] It is thus seen that in this type of iron(II) complex the absorption wavelength shifts are related to the increasing effect of the donor π-bond. The ultraviolet–visible spectra of bisdimethylglyoxime(pyridine)copper(II) resembles those of the corresponding iron(II) compound, and the same absorption ranges have been found.[63]

The influence of substituted pyridines on the ultraviolet–visible spectra of iron(II)–nioxime-pyridine complexes has been studied by Sanders and Day.[67] The solvent effect for the bisnioxime(bispyridine)iron(II) complex has also been investigated. The charge-transfer absorption bands are iron(II) → dioxime (~525 nm) and iron(II) → pyridine (~400 nm, ~295 nm). Electron-donating and electron-withdrawing substituents in the pyridine ring shift the 400-nm band to shorter and longer wavelengths respectively, relative to methyl substituents in the same position. The metal → dioxime band (525 nm) is, however, displaced in the opposite direction, thus showing an influence by the donor π-bond. The iron → pyridine absorption bands show a marked solvent effect. The iron → dioxime absorption band is only slightly affected by the solvent. The solvent effects are due to both the dielectric constant and the hydrogen-bonding power of the solvent. However, the large solvent shift for the 400-nm band may also be caused by the rotation of the pyridine rings around the z-axis, as no dissociation of the complex has been observed. Solvents more basic than pyridine have not been used.

Co(III) compounds with the composition $Co(HA)_2B_2^+$, where H_2A = α-dioxime and B = substituted anilines, have been investigated by Matsumoto *et al.*[68,69] The characteristic absorption bands are found between 300 and 375 nm, and 340 and 400 nm. The latter band is assigned to aniline → metal charge-transfer, because a linear correlation is found between the absorption frequencies and the ionization potential of the substituted aniline. The position of the band will shift when different substituted anilines are used. No effect is observed when the structure of the dioxime molecule is changed. The band between 300 and 375 nm is assigned to the metal → oxime charge-transfer and moves towards longer wavelengths in the order dimethylglyoxime < nioxime < α-benzildioxime < α-furildioxime (*cf.* the system iron(II)–dioxime–pyridine[64–66]).

The absorption spectra of palladium complexes with dimethylglyoxime, nioxime, heptoxime and α-furildioxime have been recorded in various solvents by Alimarin *et al.*[70] The spectra have been resolved into their bands and the oscillator strength of the different resolved absorption bands has been determined. For analytical purposes it may be interesting to note that the molar absorptivity of palladium α-furildioxime is considerably higher than that of the other complexes investigated.

In acid solution a neutral dimethylglyoxime molecule may be co-ordinated to a copper ion. Babko *et al.*[71] have recorded the absorption spectra of acid solutions containing dimethylglyoxime and $Cu(I)Cl$ or $Cu(II)Cl_2$. The spectra differ from those of the corresponding acid copper chloride solutions without dioxime. The complexes, proposed to be $Cu(I)H_2ACl$ and $Cu(II)H_2ACl_2$, are only formed in acid solutions. Corresponding complexes of copper(I) with other anions than chloride do not seem to be formed. Some of the lanthanides have been claimed to form similar complexes,[72] *e.g.*, $Ln(III)H_2ACl_2(H_2O)_nCl$. From the ultraviolet–visible spectral data it can be observed that the interaction between the metal and the dioxime is very weak. The difference between the spectra of the uncomplexed and the complexed species is very small both with respect to the absorption wavelengths and the intensities.

Infrared investigations of metal dioximes in solid phase and solution

Most infrared investigations have been focused on the stretching frequencies of the hydroxyl groups and the hydrogen bonds that are present in all known bivalent transition metal dioximates with the ligand to metal ratio 1:2, see *e.g.*, Blinc and Hadži,[73] Burger *et al.*,[74] Caton and Banks.[75]

A more complete assignment of the chelate ring vibrations has been made by Bigotto *et al.*[76,77] The spectra for the solid glyoxime and dimethylglyoxime complexes with some transition metals have been investigated between 4000 and 200 cm^{-1}. The assignments of the bands are done on the basis of the potential energy distribution. By this method it is found that the bands in the 2200–2700 cm^{-1} region originate from pure O—H—O stretchings and that the bands near 1700 cm^{-1} are due to almost pure O—H—O bendings. The asymmetric C═N stretching band is found between 1500 and 1600 cm^{-1} and the symmetric C═N stretching band between 1300 and 1400 cm^{-1}. These bands show, however, coupling with other vibrations, *e.g.*, C—C. Several of the vibration bands below 800 cm^{-1} are associated with the metal–nitrogen stretching mode. This is especially marked for the bands near to 500 cm^{-1}. An approximation of the force constants has been done so that good agreements are finally obtained between the observed and the calculated frequencies for all the investigated complexes. The force constants of the metal–nitrogen bonds decrease in the order Pt(II) > Pd(II) > Cu(II) > Ni(II). A comparison between the stability constants[2] of copper, nickel and palladium dimethylglyoximates shows a decrease in the same order (*cf.* Table II).

Caton and Banks[75] have made an extensive infrared study of the hydrogen bonds in copper and nickel dimethylglyoximates, nickel ethylmethylglyoximate and their deuterated analogues. The infrared spectra of the crystalline compounds and their chloroform solutions were recorded. The crystalline copper bisdimethylglyoximate has two different oxygen–oxygen distances,[40] 2·526 and 2·694 Å, and two absorption bands, 2382 and 2650 cm^{-1} respectively, have been assigned to the O—H—O stretchings. The hydrogen atom is symmetrically located between the two close oxygen atoms, but the deuterium atom is not, according to the "abnormal isotope effect".[78] A very small wavelength shift is obtained upon deuteration, because the increased bond strength will counteract the increased mass. Between the farther apart oxygen atoms both the deuterium and the hydrogen atoms are expected to be located unsymmetrically. The frequency shift in this case (from 2650 cm^{-1} to 1977 cm^{-1}) is in accordance with the increased mass. The oxygen–oxygen distances of the nickel complexes investigated are so short[44,50] (2·40 and 2·33 Å respectively) that both the deuterium and hydrogen atoms are supposed to be symmetrically located between oxygen atoms. The infrared spectrum of copper bisdimethylglyoximate in solution exhibits only one OH stretching band, which is in the same region as that for the nickel complexes. It is thus concluded that the oxygen atoms rearrange in solution and yield equal lengths for the oxygen–oxygen bonds.[75]

The infrared spectrum of crystalline copper dimethylglyoximate dichloride[42] shows two absorption bands at above 3000 cm^{-1} that can be assigned to hydroxyl stretchings of associated hydroxyl groups. The crystal structure indicates that one intermolecular hydrogen bond exists between two oxygen atoms close to each other. The other bond is an intramolecular interaction between the chlorine atom, bound to *one* copper ion, and the nearest oxygen atom that is involved in the intermolecular hydrogen bonding. The absence of a distinct C═N stretching band is puzzling and has not received a proper explanation. Mikhel'son and Evtushenko[79] have obtained the same spectrum of crystalline copper dimethylglyoximate dichloride but have given a different interpretation. They have suggested that a tautomeric transformation takes place. The hydrogen atoms should thus be attached to the nitrogen atoms and the copper ion should be co-ordinated through the oxygen atoms. The bands appearing at above 3000 cm^{-1} have, however, the same position as in dimethylglyoxime, showing the presence of associated hydroxyl groups.

Burger *et al.*[74] have recorded the infrared spectra of several metal dioximates. The nature of the hydrogen bonds and the existence of a metal → C═N donor π-bond are discussed on the basis of the data obtained for C═N and O—H—O stretchings.

Electron paramagnetic resonance investigations

Electron paramagnetic resonance (epr) can be used to determine the co-ordination in a metal complex. The epr data also give information about the covalent or the ionic character of the bonds. The method is especially advantageous when applied to copper complexes with ligands containing nitrogen atoms, because epr signals are obtained from both the copper and the nitrogen atoms. Schübel and Lutze[80] have calculated the epr parameters for copper methyl-, dimethyl- and ethylmethylglyoximate dichloride and copper bisethylmethylglyoximate, assuming the complexes to be planar. The experimental data were obtained from spectra measured at 77 K and 300 K in ethanol and pyridine. The influence of the ligand exchange can be observed in the spectra of complexes with one co-ordinated neutral dioxime molecule. The influence of the solvent can also be studied.[80] The low-temperature and room-temperature epr signals of copper bisdimethylglyoximate in different solvents have been studied by Falk *et al.*[71] The epr parameters calculated from experimental data are compared to the theoretically calculated epr parameters. Dyrssen and Hennichs[82] had earlier proposed that in a neutral aqueous solution of copper bisdimethylglyoximate two water molecules are co-ordinated to the complex and that in the pH range around 10 one proton will be removed from $Cu(HA)_2(H_2O)_2$. The epr data[71] confirm that at pH $\sim$10·5 a new species will appear, probably $Cu(HA)_2(H_2O)OH^-$ (H_2A = dimethylglyoxime). However, when the pH is increased to about 11·6, the epr data show that the chelate structure is broken and that the copper ion becomes co-ordinated to only two nitrogen atoms. The structure is probably $CuA(H_2O)_x(OH)_y^{y-}$ with $x + y \leq 4$. Above pH 14 the epr spectrum has the same characteristics as that of copper sulphate dissolved in sodium hydroxide. The signals are probably caused by $Cu(OH)_4^{2-}$. In the epr spectra of 0·1M pyridine and copper bisdimethylglyoximate in chloroform and benzene solutions where the adduct $Cu(HA)_2C_5H_5N$ is formed,[63] four equivalent couplings of dioxime nitrogen atoms to copper are discernible. The epr data show no appreciable coupling to any axial nitrogen. In order to calculate the adduct formation constant of copper bisdimethylglyoximate with pyridine in benzene,[83] the shift in the epr spectra (g-values at constant field strength) with increasing concentration of pyridine has been measured. The complex formation between molybdenum(V), obtained by reduction with tin(II), and nioxime and heptoxime was investigated by Marov *et al.*[84] They have concluded that an $MoO(HA)_2^+$ complex is formed.

Nuclear magnetic resonance investigations

The use of nmr spectroscopy to study metal dioximates has been restricted to cobalt(III) complexes. The cobalt(III) complexes of the type Co(III)$(HA)_2LX$, where H_2A = dimethylglyoxime, L = pyridine or triphenylphosphine and X = Cl^-, Br^-, I^-, CN^-, NO_2^-, Me, Et, *n*-Pr or CH_2CF_3, have been thoroughly investigated by Hill and Moralle.[85] The effect of the ligand (L) on the *cis* or *trans* position of the different anions or groups (X) was studied. The protons of dimethylglyoxime and the ligand (L) give chemical shifts that could be attributed to ground state *cis* and *trans* effects depending on the nature of the ligand X. A correlation has been found between the chemical shifts of the methyl protons and the Hammett σ_{para}-function of the ligand X, which may be related to a ground state *cis* effect due to the changes in the electron density of the *cis*-ligands in these complexes. It has been noticed by Naumberg *et al.*[86] that cobalt(III) complexes of the type Co(III)$(HA)_2RB$, where R = an alkyl group and B = a base, show a magnetic non-equivalence between the dioxime methyl groups, confirming the presence of an asymmetrical nitrogen atom.

Mössbauer investigations

Mössbauer spectroscopy has been used by Burger *et al.*[87,88] to study the structure and bonding relations of iron(II) and iron(III) complexes. The spectrum of solid iron(II) dimethylglyoximate shows that the complex must be polynuclear, as iron(II) has two bonding states. The crystals are thus built up[87] by molecules of $NaFe(HA)_2OH$ and $Fe(HA)_2$ in the ratio 2:1. The isomeric shifts of iron(II) and iron(III) dimethylglyoximate are nearly identical, showing that the *s*-electron density for both iron nuclei must be the same. The isomeric shift for the iron(II) α-furildioxime complex is smaller than for other investigated dioximes,[88] indicating that the *s*-electron density is relatively high compared with the other complexes. It has been pointed out[89] that an iron(II) spectrum must be measured under anaerobic conditions. A composite spectrum of signals from both iron(II) and iron(III) is otherwise easily obtained, like the one reported for iron(II)-salicylaldoxime.[87] The strength of the π-bond has been studied in the complexes Fe(II)$(HA)_2B_2$, where H_2A = dimethylglyoxime and B = a substituted pyridine.[90] Methyl groups in α- and γ-positions of the pyridine molecule strengthen the π-bonds by attracting the charge from the iron(II) atom. A methyl group in the β-position weakens these bonds. A greater effect is thus obtained in the spectra of the complexes with B = α- and γ-substituted pyridines than in the spectrum of the complex with B = β-substituted pyridines.

Miscellaneous investigations

A great number of composite complexes, especially of cobalt(III), have been prepared and analysed. In Table I references are given to some papers containing information on the preparation and characterization of Co(HA)XY compounds. As the aim of the investigations has often been to study the mechanism of substitution reactions, *e.g.*, the exchange of the ligands X and Y in $Co(HA)_2XY$, the determination of the structure of the compounds by the methods mentioned above is in most cases of secondary importance. With few exceptions composite complexes have not been utilized for analytical purposes. Adduct formation has, however, been used in the determination of iron(II) and cobalt(II) with dimethylglyoxime (see Table III), and Zolotov and Vlasova[91] have studied the ion-pair extraction of the Co(III)$(HA)_2$ $(pyridine)_2^+$ ion with different anions. Bearing in mind the possible analytical use of the composite cobalt(III) complexes in the future, it seems worthwhile to give a short summary of some investigations.

The associated water molecule in cobalt(III) complexes of the type $CoX(HA)_2H_2O$ with X and H_2O in *trans* positions (H_2A = dimethylglyoxime, X = Cl^-, Br^-, OH^-, NO_2^-, H_2O, NH_3 and amines) can dissociate[124,125] according to

$$CoX(HA)_2H_2O \rightleftharpoons CoXOH(HA)_2^- + H^+ \tag{9}$$

Palade *et al.*[125] have shown that the degree of dissociation is dependent on the influence of the ligand X in the *trans* position. The more *trans*-active X is, the lower the dissociation constant. The *trans* effect was found to diminish in the order $OH^- > NO_2^- > Br^- > Cl^-$. The proton may also be dissociated from the dioxime according to

$$CoXY(HA)_2^- \rightleftharpoons CoXY(HA)(A)^{2-} + H^+ \tag{10}$$

with Br^-, CN^- and NO_2^- as X and Y ligands. The dissociation constant has been determined spectrophotometrically by Birk *et al.*[126] Additional X and Y ligands (*e.g.* NH_3 and aromatic amines) have been investigated by others.[127,128] The replacement of iodine with water has been determined for dimethylglyoxime complexes with the composition $CoXI(HA)_2$, where X = Cl^-, Br^-, I^-, NO_2^-, SCN^-, N_2O. The values of the equilibrium constants for the reaction

$$CoXI(HA)_2 + H_2O \rightleftharpoons CoX(HA)_2(H_2O) + I^- \tag{11}$$

have been determined by Dubinskii.[129] The value will increase with the increasing *trans*-activity of the ligand X in the order $I^- < H_2O < Cl^- < Br^- < NO_2^- < SCN^-$.

In a recent work Burger *et al.*[130] have used $Co(HA)_2(solvent)_2^+$ as a reference acceptor for studying the donor strengths of different solvents. The iodide ion was

TABLE I.—COMPOSITE COBALT(III) COMPLEXES. THE COMPLEXES ARE *trans* UNLESS OTHERWISE STATED. ALL CHARGES ARE OMITTED.

Co(III) compound	Remarks	Ref.
Methylglyoxime		
$CoX_2(HA)_2$	X = CN, SO_3, NO_2, SCN	92
Dimethylglyoxime		
cis$[Co(OH_2)(HA)_2]$; $[Co(OH)(HA)_2H_2O]\cdot H_2O$		93
cis$[CoX(HA)_2H_2O]$; *cis*-$H[CoCl_2(HA)_2]\cdot 3H_2O$	X = I, Br, Cl, SCN	94
cis$[CoCl(HA)_2H_2O]\cdot 2H_2O$; $[CoCl(HA)_2H_2O]$	K_{a2} = *0·350 and 0·014 respectively*	94
$[CoX_2(HA)_2]$	X = I, Br, Cl; kinetics of aquation	95
$[CoCl(HA)_2NH_3]$	crystal structure *determination*	96
$[Co(CN)_2(HA)_2]$		97–99
$[Co(CN)(HA)_2H_2O]$		97
$[Co(CN)(HA)_2NH_3]$; $(NH_4)_2[Co(CN)(SO_3)(HA)_2]\cdot 4H_2O$		99
$H[CoCl(CN)(HA)_2]\cdot 4H_2O$		99
$[CoI(NCO)(HA)_2]$; $[Co(NO_2)(NCO)(HA)_2]$		100
$H[Co(NCSe)_2(HA)_2]$; $[CoX_2(HA)_2]$	*series of novel complex salts of the acid;* X = I, Br, Cl, SCN	101
$[CoX(HA)_2MeOH]$	X = I, Br, Cl, NO_2	102
$[CoX(HA)_2B]$	X = I, Br, Cl, NO_2, SCN; B = aromatic amines	103–105
$[Co(HA)_2B_2]X$	X = I, Br, Cl, NO_3, ClO_4; complex univalent anions; B = NH_3, aromatic amines	105–107
$[CoX(HA)_2Y]$; $[Co(HA)_2Y_2]X$	X = I, Br, Cl, NO_2, NCS, NO_3, ClO_4; Y = pyridine-*N*-oxide	108
$[CoX(HA)_2Y]$; $[Co(HA)_2Y_2]X$; $[Co(HA)_2Y][CoX_2(HA)_2]$	X = I, Br, Cl, SCN; Y = $NH_2C_2H_4OH$	109
$[CoX(HA)_2Y]$; $[Co(HA)_2Y_2]$	X = I, Br, Cl, NCS, NCSe; Y = selenourea, thiourea	110, 111
$[Co(HA)_2B_2][Co(SCSe)_2(HD)_2]$	B = amine; H_2D = nioxime	112

1,2-Cyclopentanedionedioxime		
$M[Co(NO_2)_2(HA)_2]$	M = *e.g.*, K, Cs, $[CoCl_2en_2]$, $[Cu(NH_3)_4]$	113
1,2-Cyclohexanedionedioxime (nioxime)		
$[CoX_2(HA)_2]$	X = I, Br, Cl	114
$M[Co(NCSe)_2(HA)_2]$	M = *e.g.*, metal ions, Co(III) ammines	112
$M[Co(NO_2)_2(HA)_2]$	M = *e.g.*, K, Cs, $[CoCl_2en_2]$, $[Cu(NH_3)_4]$	113
$Na[Co(NO_3)_2(HA)_2]$	exchange of Na	115
$NH_4[CoCl(SO_3H)(HA)_2]$	kinetics of aquation	116
$[CoX(HA)_2B]$	X = I, Br, Cl; B = amine	117
$[Co(HA)_2B_2]X$	X = Br, NO_3, ClO_4, HSO_4; B = aromatic amines	106, 118
$[Co(HA)_2B_2][Co(SCSe)_2(HD)_2]$	B = amine; H_2D = nioxime	112
α-Furildioxime		
$NH_4[CoCl(SO_3H)(HA)_2]$	kinetics of aquation	116
$[Co(HA)_2B_2]Cl$; $[CoCl(HA)_2B]$	B = aniline, pyridine, en, NO_2	119
α-Benzildioxime		
$[Co(OH)(HA)_2H_2O]\cdot 9H_2O$; *cis*$[Co(OH)(HA)_2H_2O]\cdot 4H_2O$		120
$[Co(HA)_2(H_2O)_2]$; *cis*$[Co(OH)_2(HA)_2]$	*trans*—pH ≤ 4; *cis*—pH > 8	120
$M_2[CoX(SO_3)(HA)_2]$; $Na_3[Co(SO_3)_2(HA)_2]$;	X = SCN, NO_2, amine; M = Na, $NH_4[Co(NH_3)_6]$	121
$[Co(HA)_2B_2]X$	X = I, Br, Cl, NO_3, ClO_4; B = aromatic amines	122
$[CoCl(HA)_2P(C_6H_5)_3Cl]$; $[Co(HA)_2P(C_6H_5)_3B]$	B = uracil	123

TABLE II.—STABILITY CONSTANTS FOR DIOXIMES AND THEIR METAL COMPLEXES (nomenclature as in A. E. Martell and L. G. Sillén, *Stability Constants of Metal-Ion Complexes*, Chem. Soc. Spec. Publ. No. 17, London, 1964).

Metal	Method	Medium	Log of equilibrium constant	Ref.
Methylglyoxime				
H	pot	50% dioxan–0·1*M* $NaClO_4$, 20°C	K_1 12·45, K_2 11·50	138
La(III) to Lu(III)	pot	50% dioxan–0·1*M* $NaClO_4$, 20°C	K_1 6·07 to 7·42, K_2 5·18 to 6·15, β_2 11·25 to 13·46	138
Dimethylglyoxime				
H	spectr	aq	K_1 12·05, K_2 10·54, K_{D2} −0·95($CHCl_3$)	139
H	pot	50% dioxan–0·1*M* $NaClO_4$, 20°C	K_1 13·38, K_2 12·03	138
Co(II)	pot	0·3*M* $NaClO_4$, 20°C	K_1 8·7, K_2 9·0	134
Co(III)	pot	0·3*M* $NaClO_4$, 20°C	K_1 15·0, K_2 10·0, K_3 7·2	134
Ni(II)	sol		K_{S2} −5·98(H_2O), −3·34($CHCl_3$), −4·06(C_6H_6), −4·16(CH_3CN), −4·62(EtOH), −6·60(n-C_7H_{16})	62
Ni(II)	distr	0·1*M* $NaClO_4$, 25°C	K_1 8·99, K_2 8·62, K_{D2} 2·30($CHCl_3$)	140
Ni(II)	sol	0·1*M* $NaClO_4$, 20°C	K_1 8·83, K_2 8·57, K_{S2} −6·01	141
Cu(II)	sol		K_{S2} −2·19(H_2O), −2·36(EtOH), −2·84(CH_3CN), −3·03($CHCl_3$), −4·12(C_6H_6)	62
Cu(II)	spectr	$CHCl_3$	$K(Cu(HA)_2 + B \rightleftharpoons Cu(HA)_2B)$ 2·10 (B = dibutylamine), 1·92 (B = aniline), <0 (B = TBP, hexone, CH_3SCN, $CH_2{=}CHCH_2NCS$)	63
Cu(II)	spectr	C_6H_6	$K(Cu(HA)_2 + B \rightleftharpoons Cu(HA)_2B)$ < 0 (B = triethylamine), 2·52 (B = dibutylamine), 3·62 (B = dodecylamine), 3·50 (B = pyridine)	63
Cu(II)	epr	C_6H_6, $CHCl_3$	$K(Cu(HA)_2 + B \rightleftharpoons Cu(HA)_2B$, B = pyridine) 3·25($C_6H_6$), 3·43($CHCl_3$)	83
Pd(II)	distr	1*M* $NaClO_4$, 20°C	β_2 34·3, K_{D2} 1·85($CHCl_3$), $K(Pd(HA)_2 + OH^- \rightleftharpoons Pd(HA)_2OH^-)$ 5·50	142
Pd(II)	sol		K_{S2} −4·09($C_6H_5CH_3$), −3·89(i-BuOH), −3·80(Et_2O), −3·73(n-BuOH), −3·49(C_6H_6), −3·48(i-AmOH), −3·40(CCl_4), −3·36($C_2H_4Cl_2$), −3·26($CHCl_3$)	143
La(III) to Lu(III)	pot	50% dioxan–0·1*M* $NaClO_4$, 20°C	K_1 7·42 to 8·75, K_2 6·31 to 7·57, β_2 13·73 to 16·25	138
Ethylmethylglyoxime				
H	pot, sol	0·1*M* $NaClO_4$, 25°C	K_1 12·02, K_2 10·51, K_{S2} −1·88	30
H	distr	0·1*M* $NaClO_4$, 25°C	K_{D2} −1·833(n-C_6H_{14}), −1·096(CCl_4), −0·511(C_6H_6), −0·469($CHCl_3$)	30
Ni(II)	sol	25°C	K_{S2} −5·91(n-C_7H_{16}), −5·56(H_2O), −3·88(EtOH), −3·14(CH_3CN), −2·53(C_6H_6), −1·65(CH_3Cl)	62

Ni(II)	distr, sol	0·1*M* NaClO$_4$, 25°C	β_2 17·79, K_{s2} −5·56(α-Ni(HA)$_2$), K_{s2} −4·92(β-Ni(HA)$_2$), K_{D2} 3·75(CHCl$_3$)	144
Cu(II)	distr	0·1*M* NaClO$_4$, 25°C	K_1 9·03, K_2 10·64, K_{D2} 0·535(CHCl$_3$), K(2Cu(HA)$_2$(CHCl$_3$) $\rightleftharpoons$ (Cu(HA)$_2$)$_2$(CHCl$_3$))2·1	145
Cu(II)	sol	0·1*M* NaClO$_4$, 25°C	K_{s2} −1·79(CHCl$_3$), −2·02(EtOH), −2·73(0·1*M* NaClO$_4$), −3·19(C$_6$H$_6$), −4·57(CCl$_4$)	145
Methylacetylglyoxime				
H	pot	50% dioxan–0·1*M* NaClO$_4$, 20°C	K_1 11·24, K_2 10·17	138
La(III) to Lu(III)	pot	50% dioxan–0·1*M* NaClO$_4$, 20°C	K_1 4·98 to 6·42, K_2 4·02 to 5·23, β_2 9·00 to 11·56	138
1,2-*Cyclohexanedionedioxime* (*nioxime*)				
H	spectr	aq	K_1 12·16, K_2 10·70, K_{s2} −2·08(CHCl$_3$), K_{D2} −0·94(CHCl$_3$)	139
H		1·0*M* 20°C	K_2 10·83	146
H		20°C	K_{s2} −1·31(1*M* NaClO$_4$), −3·3(C$_6$H$_6$)	147
H	pot	0·2*M* NaNO$_3$	K_2 9·59	148
Fe(III)	distr	0·5*M* NaClO$_4$	K_1 11·07, K_2 10·67, K_3 10·25, K_{D3} 1·98(CHCl$_3$), K_{D3} 0·39(N-AmOH)	149, 150
Ni(II)	distr	0·1*M* NaClO$_4$, 25°C	K_1 11·03, K_2 10·59, K_{D2} 2·15(CHCl$_3$)	140
Ni(II)	sol	1·0*M* 20°C	K_1 11·99, K_2 10·74, K_{s2} −6·48	146
Cu(II)	pot	0·2*M* NaNO$_3$ 21°C	K_1 9·99, K_2 9·39	148
Pd(II)	distr	1·0*M* NaClO$_4$	K_{D2} 0·5(C$_6$H$_6$), K(Pd(HA)$_2$ + OH$^-$ $\rightleftharpoons$ Pd(HA)$_2$OH$^-$) 3·8	147
1,2-*Cycloheptanedionedioxime* (*heptoxime*)				
H	spectr	aq	K_1 12·21, K_2 10·65, K_{s2} −1·72(CHCl$_3$), K_{D2} −0·70(CHCl$_3$)	139
H	spectr	1·0*M* NaClO$_4$, 20°C	K_1 12·15, K_2 10·70	151
Ni(II)	distr	0·1*M* NaClO$_4$, 25°C	K_1 11·24, K_2 10·68, K_{D2} 2·18(CHCl$_3$)	140
Ni(II)	sol	0·1*M* NaClO$_4$, 20°C	K_1 10·77, K_2 10·39, K_{s2} −5·85	141
Pd(II)	distr	1·0*M* NaClO$_4$	β_2 43·00, K(Pd(HA)$_2$ + OH$^-$ $\rightleftharpoons$ Pd(HA)$_2$OH$^-$) 3·3	151
Phenylglyoxime				
H	pot	50% dioxan–0·1*M* NaClO$_4$, 20°C	K_1 12·70, K_2 11·72	138
La(III) to Lu(III)	pot	50% dioxan–0·1*M* NaClO$_4$, 20°C	K_1 6·38 to 7·67, K_2 5·52 to 6·54, β_2 11·90 to 14·09	138
α-*Furildioxime*				
H		aq 20°C	K_2 10·26, K_{s1} −2·08	152
H	spectr	0·1*M* 25°C	K_1 11·25, K_2 9·84, K_{s2} −2·32(CHCl$_3$), K_{D2} −0·45(CHCl$_3$)	139
H		1·0*M* NaClO$_4$, 20°C	K_1 11·53, K_2 9·86, K_{s2} −2·57(1*M* NaClO$_4$),	

TABLE II.—(*contd.*)

Metal	Method	Medium	Log of equilibrium constant	Ref.
H	pot	aq	K_{S2} $-3{\cdot}35(C_6H_6)$	147
Ni(II)	distr	0·1*M* $NaClO_4$, 25°C	K_1 10·6, K_2 9·50, K_{S2} $-2{\cdot}00$	38
Pd(II)		1·0*M* $NaClO_4$	K_1 8·18, K_2 6·67, K_{D2} $2{\cdot}18(CHCl_3)$	140
			β_2 43·72, $K(Pd(HA)_2 + OH^- \rightleftharpoons Pd(HA)_2OH^-)$ 3·3	147
α-Benzildioxime				
H		0·1*M* 25°C	K_2 10·10	153
H	spectr	1·0*M* $NaClO_4$	K_1 11·91, K_2 10·29	154
Ni(II)		0·1*M* 25°C	β_2 26·20	153
Cu(II)	distr	0·05*M* Cl^-	$K(Cu^{2+} + 2H_2A(org) \rightleftharpoons Cu(HA)_2(org) + 2H^+)$ $-6{\cdot}8(C_6H_6)$	155
Pd(II)	distr	1·0*M* $NaClO_4$	β_2 34·6, K_{D2} $2{\cdot}3(C_6H_6)$, $K(Pd(HA)_2 + OH^- \rightleftharpoons Pd(HA)_2OH^-)$ 4·8	154

TABLE III.—ANALYTICAL PROCEDURES USING DIOXIMES FOR DETERMINATION OF TRANSITION METALS. APPLICATIONS GIVEN IN PARENTHESES.

Dioxime	Method	Range, precision	Procedure, interferences, remarks (material analysed)	Ref.
a. Manganese, Mn(II)				
dmg	spectr. 350 nm			175
furil	spectr. 380 nm			175
b. Rhenium, Re(VII)				
dmg	spectr. 445 nm	5–25 ppm	~0·5*M* HCl, redn. of ReO_4^- w. $SnCl_2$; Mo, Pt, W interf. (refractory alloys)	176
dmg	spectr. 440 nm	1–100 µg	ReO_4^- extd. w. pyridine, anion-exchange, traces of Mo, W eluted w. oxalate,	177
		1–10 ppm, 8%	ReO_4^- eluted w. $HClO_4$; dmg and $SnCl_2$ added (Mo and W ores, flue-dusts)	
dmg	spectr. 445 nm	1–20 ppm	~1*M* HCl, redn. w. $SnCl_2$, W mask. w. tartr. (W alloys)	178
niox	spectr. 440 nm	20–50 ppm	~0·6*M* HCl, redn. w. $SnCl_2$ (refractory alloys)	176
furil	spectr. 530 nm	0·5–200 µg	~1*M* HCl, redn. w. $SnCl_2$ (Mo ore)	179
furil	spectr. 532 nm	20–200 µg	HCl, HF; F^- mask. w. borate, redn. w. $SnCl_2$ (Ta–Re alloys)	180
furil	extn. spectr. 530 nm	1–5 ppm	~1*M* HCl, redn. w. $SnCl_2$, extn. $CHCl_3$; Pd, Mo interf. (refractory alloys)	176
c. Iron, Fe(II)				
dmg	extn. radiom.	10^{-4}–10^{-8}*M*, 95–97% extn	pH 8–9, pyridine added, extn. w. $CHCl_3$; Fe(III) mask. w. tartr. <1% extd.	181
d. Cobalt, Co(II)				
glyox	spectr. 285–290 nm	0–4 ppm	pH 8·0–9·5; Cu, Ni, Fe(III) mask. w. EDTA	182
3-methyl-glyox	spectr. 260·5 nm	0–7 ppm	pH 8·0–9·5; Cu, Fe(III), CN^-, SCN^- interf.	183
dmg	spectr. 435 nm	0·2–2 ppm	pH 4·5–5·0; KI add., $Co(HA)_2I_2^{2-}$ formed Ag, Al, Bi, Fe, Hg, Ni, Pb interf., can be masked (metals)	184
dmg	polar	3–50 ppm	pH 6, stand. addn. of Co	35
furil	spectr. 350 nm	0–4 ppm	pH 8 ± 0·5; Cu, Ni, Fe(II), Pb, Ag interf. <700 ppm Na, K, Mg, Cl negl.	185
e. Nickel, Ni(II)				
dmg	extn., radiom. ^{63}Ni	0·6–3 ppm, 97% extd	rgt. from diacetyl monoxime + hydroxylamine, extn. w. $CHCl_3$, pH 8·7–9; <0·1% Pd extd.	186
dmg	extn., spectr. 262 nm	0·5 µg	extn. w. $CHCl_3$; interf. mask. w. tartr.	153
dmg	extn., spectr. 442 nm	0·5–40 ppb, 1·5–7%	extn. w. $CHCl_3$, back-extn. w. HCl, $Ni(HA)_2$ oxd. by Br_2, pH raised to 10·4; Cu and Co no interf. (sea-water)	187
dmg	extn., spectr. 445 nm	0·2–2 ppm	extn. w. $CHCl_3$ fr. citr. soln, pH 9, back-extn. w. HCl, $Ni(HA)_2$ oxd. alk. soln (W and WO_3)	188

TABLE III.—(*contd.*)

Dioxime	Method	Range, precision	Procedure, interferences, remarks (material analysed)	Ref.
dmg	pptn. (PFHS)	0·5–200 mg	rgt. from diacetyl + hydroxylamine, pH 7·1, excess of rgt. not formed	189
dmg	pptn. (PFHS)		Fe mask. w. tartr., small amt. of Co no interf.	190
dmg	pptn. (PFHS)		rgt. from diacetyl + hydroxylamine, quant. pptn. pH 5–12; Pd copptd.	55
dmg	pptn. (PFHS)	~30 mg	methods of mask. interf. fr. Fe, Co, Cu, detn. of Ni(IV) (iron and steel)	191
dmg	pptn., polar	23–411 ppm	pptd. $Ni(HA)_2$ dissolved in 6*M* HCl, a.c. polar. 1·15 V in HCl-tartr. soln	192
dmg	copptn., polar. DME	5–15 ppm	pptd. $Ni(HA)_2$ dissolved, pH 1·5–2, stand. add. of Ni	35
dmg	copptn., (PFHS)	3–7 mg	copptn. w. $Pd(HA)_2$, pH 7–8	186
dmg	copptn.	0·06–6 ppm	copptn. of Ni w. $Mg(OH)_2$ in presence of dmg	193
dmg	titn. extern. indic.	~0·06 g, 2%	titn. w. H_2A, pH 8, Cu mask. w. thiourea, Co(II) and Fe(III) interf. (alloys)	194
dmg	spot test	3–6 ppm	NaAc soln, interf. ions mask.	195
dmg	mass spectr.	$0·1–10^{-8}$ μg $Ni(HA)_2$		196
4-t-butyl-niox	extn., spectr. 386 nm	3–10 ppm	pH ~7, extn. w. xylene, Ce(IV), Cr(III), Cu, Mn, Sn(IV) Ti(IV), V(V) interf., can be mask.; sepn. from Co(II) ion-exchange (Sc, Y, La to Lu)	197
C_8–C_{12} cycl. 1,2-dionedioxime	pptn.	Ni >10 mg	pH 5–6, cyclo-octane 1,2-dionedioxime most useful; interf. not studied	5
hept	extn. spectr.		tartr. or citr. medium (silica minerals, Ge, Zr and Cd salts, In and Ga metals)	198
hept	extn., spectr. 377 nm	1–5 μg	pH 2·7–12·4, extn. w. $CHCl_3$	199
furil	extn., spectr.		see detn. w. hept	198
furil	extn., spectr. 435 nm	5–15 μg, 3%	Ac-tartr.-borate soln. pH ~9, extn. w. $CHCl_3$; Co and Cu interf. (rocks, soils, steels, biol. mat., fats)	200
furil	extn., spectr.		extn. w. $CHCl_3$ from ammoniacal, citr. or tartr. solns for optim. extn.	201
furil	copptn., spectr. blue filter	1–10 μg	copptn. $Ni(HA)_2$ and 2,4-dinitroaniline, ppt. dissolved, oxd. w. $S_2O_8^{2-}$, NaOH add., (nat. matr.)	202
benzil	extn., spectr.		see detn. w. hept	198
f. Palladium, Pd(II)				
glyox	extn. spectr. 397 nm	0·1–0·5 mg	pH 1; Au, Fe, Ir, Pt, PO_4^{3-} mask. w. EDTA	203
dmg	extn. spectr. 295, 370 nm	25–800 μg, 3–7%	pH −0·6 to 2, $CHCl_3$; Ag, Cu, Ni, Pb no interf.	143

TABLE III.—(*contd.*)

Dioxime	Method	Range, precision	Procedure, interferences, remarks (material analysed)	Ref.
dmg	pptn. (PFHS)	1–200 mg	rgt. from diacetyl + hydroxylamine, pH 0·4; excess of rgt. not formed	189
dmg	pptn. (PFHS)		rgt. from diacetyl + hydroxylamine, quant. pptn. pH 1–8; Ni copptd.	55
dmg	copptn. (PFHS)	3–7 mg	rgt. from diacetyl or diacetyl monoxime + hydroxylamine, copptd. w. ~30 mg Ni	186
dmg	copptn., spectr. 452 nm	50 μg	copptn. w. ~2 mg Ni, pH 6·5, dissolved ppte. extd. w. dithizone–CCl_4	204, 205
niox	copptn., (PFHS)	1–50 mg	rgt. from 1,2-cyclohexanedione + hydroxylamine, 0·3–1*M* HCl; Co, Cu, Ni, Pt no interf.	206
niox	amp. titn.	10^{-3}–10^{-4}*M*, 1·5%	rot. Pt-electrode	207
C_8–C_{12} cycl. 1,2-dionedioxime	pptn.	>6 mg	see detn. of nickel, Table III*e*.	5
benzil	spectr. S 42 filter	0·2–2 ppm	Al, Ca, Cd, K, Mg, Na, NH_4, Cl^-, NO_3^-, SO_4^{2-} no interf.	208
benzil	pptn.	1–100 μg	copptn. with excess of rgt. in 0·5*M* HCl, sepn. fr. Pt, Ir, Rh, Ru	209
g. Copper, Cu(II)				
dmg	polar	1–10 ppm	detn. of Cu copptd. (not quant.) w. $Ni(HA)_2$, dissolved in HCl, a.c. polar. −0·25 V in tarr. soln.	192
furil	extn. spectr. 445 nm	0·25 mg	extn. w. $CHCl_3$, pH 9·5; Cu sepd. from Co and Ni by back-extn. w. H_2SO_4, pH raised to 9·4 and extn. w. $CHCl_3$; Al, Fe, Ti mask. w. tartr. (silicate rocks, ores, minerals)	210
h. Bismuth, Bi(III)				
niox and subst. niox	pptn.	50–500 mg	pH 9–12; Ag, Cd, Co, Cu, Hg, Ni, Pd, Zn interf. mask. w. CN^-	5

found to be the most advantageous ligand for the displacement of the solvent molecules. The substitution of the first solvent molecule, according to

$$Co(HA)_2S_2^+ + I^- \rightleftharpoons CoI(HA)_2S + S \tag{12}$$

where S denotes the solvent molecule, is promoted by the electrostatic interaction between the iodide ion and the complex cation. The equilibrium constant for equation (12) can be correlated with the donor strength of the solvent. The displacement of the second solvent molecule according to

$$CoI(HA)_2S + I^- \rightleftharpoons CoI_2(HA)_2^- + S \tag{13}$$

can be related to the dielectric constant of the solvent. The dissociation of $CoI_2(HA)_2^-$ will increase with increasing dielectric constant, mainly on the basis of the easier solvation of the iodide ion. Several dioximato compounds of rhodium(III) have been prepared in analogy with the corresponding cobalt(III) complexes.[131–133] The similarity in the X-ray diffraction patterns of $[M(HA)_2(NH_3)_2]Cl{\cdot}5H_2O$ where H_2A = dimethylglyoxime and M = Co, Rh, indicates that the compounds are isostructural.[132] The dissociation constant in aqueous solution for the reaction

$$[Rh(HA)_2(NH_3)_2]^+ \rightleftharpoons Rh(HA)(A)(NH_3)_2 + H^+ \tag{14}$$

has been determined.[131] The value is $\log K = -7{\cdot}10$, which is considerably higher than the value for the corresponding cobalt(III) compound ($-10{\cdot}5$ according to Yamano *et al.*[127]).

When the mixed complex between Co(II), dimethylglyoxime and the anions Cl^-, Br^-, I^- and SCN^- is formed, only one proton is removed.[134,135] The composition is $CoX_2(HA)(H_2A)^-$, whereas it is[135] $CoX_2(HA)_2^-$ for X = $SeCN^-$. In a similar study of Fe(II) only the complexes with the composition $FeX_2(HA)_2^-$ have been found. The stability constants for both Co(II)-and Fe(II)-dimethylglyoxime-X complexes increase in the order $Cl^- < Br^- < I^- < SCN^- < SeCN^-$. The co-ordination of SCN^- and $SeCN^-$ is believed to take place through the sulphur and selenium atoms,[135] because in the infrared spectra of the complexes the C≡N stretching band appears at increased frequencies in the order $SCN^- < Co(SCN)^+ < CoSCN(HA)_2^-$. A co-ordination through the nitrogen atom should cause a decrease of the C≡N frequency. The same behaviour has been found for the corresponding complexes with $SeCN^-$. When $Co(II)(HA)_2$ is oxidized in aqueous solution, a cobalt(III) complex with Co:HA^- ratio 1:3 is formed.[136] Spectrophotometric data have shown that $Co(HA)_3$ does not co-ordinate SCN^- and hence the oxidation of $Co(HA)_2$ to a Co(III) complex can be inhibited by the addition of SCN^-. It is believed that the oxidation takes place through the complex $CoOH(HA)_2^-$, which is less readily formed than the compound.

$Co(SCN)_2(HA)_2^{2-}$.

The stability constants for the following reactions between cobalt(II) and dimethylglyoxime or nioxime have been determined for different ionic strengths.[137]

$$Co(HA)(H_2A)^+ + I^- \rightleftharpoons CoI(HA)(H_2A) \tag{15}$$

$$CoI(HA)(H_2A) + I^- \rightleftharpoons CoI_2(HA)(H_2A)^- \tag{16}$$

As the iodide ions replace co-ordinated water molecules, the stability constants can be correlated to the water activity (ionic strength). The values of $\log K_1$ for equation (15) increase with increasing ionic strength, *i.e.*, the water molecule is more easily substituted at low water activity.[137] The formation of a neutral complex probably also promotes the co-ordination of the first iodide ion. The ratio between the stability constants K_1 [equation (15)] and K_2 [equation (16)] increases with increasing ionic strength. The co-ordination of the second iodide ion to form the negatively charged complex $CoI_2(HA)_2^-$ may be hindered by the increasing concentration of anions.

THE SOLUTION CHEMISTRY OF METAL DIOXIMES

Formation constants

The selectivity of a dioxime can be interpreted in terms of the stability constants for the metal complexes. The following reactions may be considered in addition to the H_2A equilibria:

$$M^{2+} + HA^- \rightleftharpoons MHA^+ \tag{17}$$

$$MHA^+ + HA^- \rightleftharpoons M(HA)_2 \tag{18}$$

$$M(HA)_2(s) \rightleftharpoons M(HA)_2 \tag{19}$$

$$M(HA)_2(aq) \rightleftharpoons M(HA)_2(org) \tag{20}$$

The equilibrium constants are K_1 $(= \beta_1)$, K_2, K_{s2} and K_{D2} respectively. The techniques used for the determination of the constants are, *e.g.*, potentiometric titration, spectrophotometric determination, solubility and distribution experiments. Sometimes competing equilibria with other ligands are used.

Dyrssen[2] has made a compilation of the stability constants for dioximes and their metal complexes up to 1964. In Table II the values of the stability constants determined since 1964 are given for the most common *vic*-dioxime complexes.

Table II shows that the values of K_1, K_2 and β_2 $(= K_1K_2)$ for the metal complexes change with the dioxime. Generally it can be said that the value of K_2 is higher than statistically expected, owing to the stabilization brought about by the formation of the hydrogen bonds (Fig. 1). The relative distribution of the metal species in solution with various concentrations of dioxime anions is shown in Fig. 3. It is evident that in the case when $K_1 < K_2$ the range for $M(HA)^+$ is rather small compared to the ranges

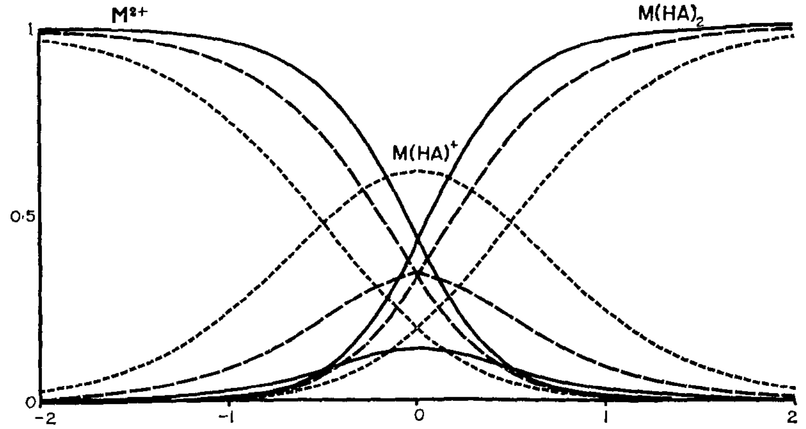


FIG. 3.—The distribution of the species M^{2+}, $M(HA)^+$ and $M(HA)_2$ as a function of $\log v = \log [HA^-] + \frac{1}{2} \log \beta_2$.

———— $\beta_1^2/\beta_2 = K_1/K_2 = 0{\cdot}1$

— — — $\beta_1^2/\beta_2 = K_1/K_2 = 1$

-·-·-· $\beta_1^2/\beta_2 = K_1/K_2 = 10$

for M^{2+} and $M(HA)_2$. This means that the separate determination of K_1 and K_2 is difficult to carry out accurately, and that the dominating reaction, with excess of dioxime anion, can be expressed as

$$M^{2+} + 2HA^- \rightleftharpoons M(HA)_2 \qquad (21)$$

with the equilibrium constant β_2. This will simplify the treatment of dioxime equilibria in analytical chemistry, since only one complex needs to be considered.

The thermal stability of some metal dioximes has been investigated by Burger *et al.*[156] The results show that the stronger the co-ordinate bond is, the lower is the initial decomposition temperature. This shows that the metal–nitrogen bonds in the chelate ring do not rupture first, but some other bond weakened by the co-ordinate bond. A comparison between the thermal stability and the value of log β_2 is, however, only possible for metal complexes with the same dioxime.

Solubility

The marked difference in the solubilities of metal dioximes in aqueous solution, especially nickel and palladium *vs.* copper dimethylglyoximate, has met with much interest. The low solubilities and solubility products of the nickel and the palladium complexes in water have often been related to metal–metal bonds in the crystals.[43,44,51,57,62] A determination of the solubilities in water of α- and β-nickel ethylmethylglyoximates has shown that α-nickel ethylmethylglyoximate, in spite of its longer nickel–nickel distance, has a lower solubility than β-nickel ethylmethylglyoximate.[144] This supports the view that the solubility is more dependent on the crystal packing[54] than the proposed intermolecular metal–metal bonds.[44,51] The distance between two successive molecular planes decreases in the order β-nickel ethylmethylglyoximate, α-nickel ethylmethylglyoximate and nickel dimethylglyoximate. The aqueous solubility of the complexes diminishes in the same order. On the basis of these data an attempt has been made to express the aqueous solubility of nickel dialkyldioximates (R and R′ being alkyl groups in Fig. 1) as a function of the distance between the molecular planes and the number of CH_2 groups in the complex.[144] It is suggested that the forces between the molecular planes can be neglected when the interplanar distance is more than 4 Å. The solubility would then depend mainly on the number of CH_2 groups.

The effect on the solubility of metal dioximates due to the ligand, the metal and the solvation power of the solvent has been discussed for the copper and nickel complexes of dimethylglyoxime and ethylmethylglyoxime.[145] The decrease in solubility noted for copper bisethylmethylglyoximate in water compared to copper bisdimethylglyoximate may be explained by the increased hydrophobic character of the ligand, which should diminish the adduct formation with water that has been shown to occur for copper bisdimethylglyoximate.[81,82] The "loosening" effect in the solid phase caused by the increased number of CH_2 groups is discernible in the nickel complexes, because nickel dimethylglyoximate has a lower solubility than nickel ethylmethylglyoximate in all solvents studied.[62] Further increase in the number of CH_2 groups will, however, probably decrease the aqueous solubility, in spite of the "loosening" effect.[144]

It can be noted that palladium complexes can be precipitated from acid solutions owing to the very high formation constants and the low solubility constants. A gradual rise in pH will, however, increase the solubility, as the hydroxy-complex

$Pd(HA)_2OH^-$ is formed.[157]

$$Pd(HA)_2 + OH^- \rightleftharpoons Pd(HA)_2OH^- \qquad (22)$$

A similar reaction occurs with the copper complexes[82] but not with the nickel complexes.

Distribution

The distribution constant can be estimated from the ratio of the solubilities in organic solvents and water. Chloroform is usually chosen as organic solvent for the extraction of metal dioximates, owing to its ability to form hydrogen bonds with the oxygen and nitrogen atoms of the oxime groups. The extraction of nickel is easily carried out from neutral or slightly alkaline solutions with the dioximes mentioned in Table II. No water molecules are associated with the nickel complexes with dimethylglyoxime and α-benzildioxime in the chloroform phase.[158] Palladium is best extracted from acid solutions,[142,157] thus avoiding the formation of $Pd(HA)_2OH^-$ and any interference from copper and nickel. The distribution constant is lower for palladium dimethylglyoximate than for nickel dimethylglyoximate, which may be due to a slight tendency of $Pd(HA)_2$ to co-ordinate water molecules.

The distribution constants determined for copper dioximates are rather low, owing to the solvation of $Cu(HA)_2$ in the aqueous phase (adduct formation with H_2O). For copper the distribution constant for the ethylmethylglyoxime complex is higher than would be expected from the constant for the dimethylglyoxime complex. The introduction of two CH_2 groups[11] should increase $\log K_{D2}$ by 1·2, but the observed difference is 1·47. This may be attributed to the lower solvation of copper bisethylmethylglyoximate in the aqueous phase. When the total concentration of copper exceeds 0·33mM, the extraction is markedly increased by the dimerization of the copper complex in the organic phase.[145]

The solvent extraction of Cu(II) with α-benzildioxime into benzene has been investigated by Einaga and Ishii.[155] Two neutral extractable complexes have been found with metal to ligand ratios 1:1 and 1:2. The 1:1 complex is formed with excess of copper and can only be extracted in the presence of ammonium nitrate. The extracted species might thus be the ion-pair $Cu(HA)^+NO_3^-$. The 1:2 complex is formed with an excess of dioxime and the extraction constant K_{ex} ($= K_{D2}\beta_2K_{a1}{}^2K_{D2}{}^{-2}$) has been determined for the reaction

$$Cu^{2+} + 2H_2A(org) \rightleftharpoons Cu(HA)_2(org) + 2H^+ \qquad (23)$$

The iron(III) complex with nioxime can be extracted with chloroform or n-pentanol, but the overall reaction is very slow.[149,150] The extraction curves for the two solvents are quite different, but in both cases the extracted compound is supposed to be Fe(III)$(HA)_3$. The possibilities that iron is reduced and extracted as $Fe(HA)_2$ by chloroform or is extracted as an ion-pair $Fe(HA)_2{}^+ClO_4{}^-$ with n-pentanol have, however, not been considered.

Adduct formation

The ability of copper complexes to form adducts in the organic phase can be used to increase the distribution of copper. Hitherto only the adduct formation with copper bisdimethylglyoximate has been investigated.[63,82] Chloroform and benzene have been used as organic solvents. The difference in the formation of adducts with pyridine, aniline and aliphatic amines is minor.[63] The formation seems, however, to be sterically hindered for tertiary amines.

It is well known that complex formation between iron(II) and dioximes takes place. The simple compound iron(II) dimethylglyoximate has, however, not been isolated. On the other hand, if an organic base is added to a solution containing iron(II) and a dioxime, isolation of the resulting compound can readily be achieved. The complex formation and extraction in the iron(II)–dioxime–amine (ammonia) system have been studied by Babko and co-workers.[65,66] The iron(II) complexes with dimethylglyoxime and nioxime can be extracted from pyridine solution with chloroform, but not from ammoniacal solution.[65,66] Spectrophotometric measurements indicate that the equilibrium in aqueous solution containing dimethylglyoxime, ammonia, pyridine (py) and iron(II) is

$$\mathrm{Fe(HA)_2(H_2O)py + NH_3 \rightleftharpoons Fe(HA)_2(H_2O)NH_3 + py} \qquad (24)$$

The extracted complex is probably $\mathrm{Fe(HA)_2(py)_2}$. The iron(II) complexes with α-benzildioxime[66] and α-furildioxime[159] are best extracted from ammoniacal solutions. The addition of pyridine will in this case lower the extraction, in contrast to the extraction of iron(II) dimethylglyoximate. Bases other than ammonia and pyridine do not give extractable compounds. The results thus indicate that only ammonia and pyridine can enter the co-ordination sphere of the complex,[66] probably for steric reasons.

Some reactions of metal dioximes in solution

In the gravimetric determination of, *e.g.*, nickel as nickel dimethylglyoximate the use of precipitation from homogeneous solution (PFHS) gives more perfect and larger crystals than those prepared by conventional methods.[160,161] In the reaction sequence[162] diacetyl + hydroxylamine → diacetyl monoxime $\xrightarrow{+\text{hydroxylamine}}$ dimethylglyoxime $\xrightarrow{+\mathrm{Ni}^{2+}}$ [yellow soluble complex] ⟶ red nickel dimethylglyoximate precipitate, a yellow colour appears, which is normally not obtained in conventional precipitation. The yellow species can be extracted with chloroform. The ultraviolet–visible absorption spectrum of the yellow chloroform solution is the same as that of the conventionally formed nickel dimethylglyoximate dissolved in chloroform. The yellow colour is assumed to be caused by undissociated nickel dimethylglyoximate, a "monomeric" species which can be present in concentrations several hundreds times the equilibrium concentration just before the formation of the red precipitate.[163] Boiling of the red precipitate in ammoniacal solution gives the yellow colour, *i.e.*, separated molecules are supposed to exist. An explanation of this behaviour based on the ligand field theory is given by Magee and Gordon[162] and the statements have been verified experimentally.

Yellow soluble nickel complexes with glyoxime, dipyridyl- and dihydroxyglyoxime can be formed in ammoniacal solution.[164] An anionic form of nickel dihydroxyglyoximate, $\mathrm{Ni(HA)_3^-}$, is suggested on the basis of data obtained by the method of continuous variation. Though an octahedral configuration is unlikely for a nickel–dioxime complex, this has been suggested for $\mathrm{Ni(HA)_3^-}$. As dihydroxyglyoxime is a considerably stronger dibasic acid[164] ($pK_{a1} = 6{\cdot}81$ and $pK_{a2} = 8{\cdot}66$) than dimethylglyoxime[139] ($pK_{a1} = 10{\cdot}57$ and $pK_{a2} = 12{\cdot}05$), alternative explanations to $\mathrm{Ni(HA)_3^-}$, *e.g.*, $\mathrm{Ni(HA)A^-}$, should be tested.

When an oxidant is added to nickel dimethylglyoxime in alkaline solution an intense red colour will appear.[1,165] The reaction is complicated to explain, as both the dioxime and the nickel ion can be oxidized. Polarographic investigations have shown that a reversible two-electron reaction[164,166–168] takes place. The nickel ion is supposed to be in a quadrivalent state in the oxidized nickel dimethylglyoxime complex. The highest ligand to metal ratio found (3:1) was determined spectrophotometrically.[164,166]

Ion-exchange studies indicate that in alkaline solution with the total concentration of $H_2A >$ the total concentration of Ni^{2+}, both neutral and doubly charged anionic complexes are present, as NiA_2 and $NiA_3{}^{2-}$ respectively. The formation constant for the reaction

$$NiA_2 + A^{2-} \rightleftharpoons NiA_3{}^{2-} \tag{25}$$

has been determined[169] to be $\log K_3 = 3{\cdot}02$.

In the preparation of red oxidized nickel dimethylglyoximate in 0·1–1M potassium hydroxide, a yellow colour appears before the oxidation starts. If no oxidant is added and the reaction solutions are kept free from air, the yellow colour persists, and nickel remains in oxidation state two. The solution is supposed to contain 1:1, 1:2 and 1:3 species of $Ni^{2+}:A^{2-}$ in equilibrium.[170] The yellow solution can be oxidized by air,[170] PbO_2[166] and iodine.[168] When iodine is used, the red solution is formed only when iodine is present in the minimum molar ratio $Ni:H_2A:I_2 = 2:6:5$. Polarographic studies have shown that dimethylglyoxime reacts with iodine in the ratio 2:1, and that a compound that can be isolated appears before the reaction with nickel will take place. The iodine is, however, not likely to be a part of the red oxidized complex.[168]

In a recent work Ksenzhek *et al.*[171] have studied the absorption of oxygen by alkaline solutions of nickel dimethylglyoximate. An absorption of oxygen, which can be removed by physical methods, takes place first, and is followed by an irreversible oxidation when the original complex decomposes. The results do not show any oxidation of the nickel ion.

The hydroxyl protons in copper and nickel dimethylglyoximates have been reported to be very unreactive towards methylmagnesium iodide.[172,173] This has been claimed to be due to the formation of strong hydrogen bonds. A recent investigation by Uhlig and Dorn[174] shows that methylmagnesium bromide does react with the hydroxyl groups in metal dioximates. Methane is evolved quantitatively if the metal complex is dissolved in xylene or pyridine. No reaction occurs if the metal dioxime is in the solid state (or suspended in a liquid).

ANALYTICAL PROCEDURES BASED ON DIOXIME REAGENTS

In Table III the determinations of some metals have been listed together with condensed information on the type of dioxime, method, range of metal concentration and precision, interferences, applications, *etc.*

The analytical problems that have been solved and the techniques that have been used can briefly be summarized as follows. Dioximes have mostly been used for the determination of nickel and rhenium in for example metals, minerals, ores, rocks, soils and biological materials. The nickel complex is usually determined after prior separation either by precipitation or chloroform extraction, *i.e.*, the low solubility of the nickel complex in aqueous solution is utilized. It has been noted that when nickel is precipitated in the presence of cobalt and iron,[191] precaution must be taken against the oxidation of nickel(II) to nickel(IV). The dioxime should thus be added to an acidified solution at $\mathrm{pH} < 4$, which is then made slightly ammoniacal. The precipitate can be dissolved in acid and analysed by, *e.g.*, Rollet's method,[211] extraction or titration procedures. The determination of nickel by extraction can be made rather specific by the use of masking reagents and a carefully chosen pH. The final determination is preferably carried out spectrophotometrically because of the higher sensitivity obtained. Either the organic phase is used directly or Rollet's method[211] applied, after a back-extraction from the organic phase. Rhenium is determined spectrophotometrically by the sensitive reaction in acid solution between perrhenate, reduced with stannous chloride, and an added dioxime. The serious interferences caused by molybdenum and platinum seem to be best avoided by extraction with pyridine followed by ion-exchange.[177] These comments show that no really new method has appeared in the determination of metals with dioximes.

Several of the procedures quoted in Table III do not deal with any special analytical problems, but are included because the reactions investigated can be used for different analytical purposes, as often suggested by the authors. Some of these works will be mentioned in the following. Precipitation from homogeneous solution (PFHS) makes it possible to handle up to 200 mg of metal in the sample compared with 30 mg usually recommended in the conventional precipitation of nickel and palladium.[189] Small amounts of nickel and palladium dioximates can be separated by co-precipitation with various compounds, *e.g.*, metal dioximates,[55,186,204,205] magnesium hydroxide[193] and 2,4-dinitroaniline.[202] Studies of the precipitation of nickel have shown that, owing to supersaturation,[163] the procedure is not quantitative for nickel unless amounts of more than 0·5 mg are used. Trace amounts of nickel as nickel dimethylglyoximate[196] can be detected by mass spectrometry. However, the quantitative determination may be a problem, owing to difficulties in the standardization. Several spectrophotometric methods have been devised for cobalt, iron and manganese, using different dioximes,[175,182,183] though the applications have not been fully outlined.

Dioximes have also been used in the analysis of other compounds than those containing transition metals. The reaction between rhenium and α-furildioxime has been applied to an indirect spectrophotometric determination of 3–5 ppm of nitrate.[212] Perrhenate and nitrate form a complex that is not reducible by stannous chloride in acid medium. Excess of rhenium is reduced and complexed with α-furildioxime. Urea in small amounts can be determined in blood[213,214] and urine[213] by the colour reaction with dimethylglyoxime in strongly acid solution. The advantage is that only small volumes are required for the quantitative determinations.[214]

Some reactions not used for analytical determinations are, *e.g.*, the increased extraction of copper and iron(II) bisdimethylglyoximates when an adduct-former is added to the organic phase, and the extraction of anions as ion-pairs with cobalt(III) and iron(III) bisdimethylglyoximate cations or *vice versa.* An ion-exchange resin has been prepared by condensation of α-furildioxime with formaldehyde and phenol.[215] The following transition metals can be sorbed from different media, $\mathrm{Pd^{2+}}$ (0·1*M* hydrochloric acid), $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, $\mathrm{Zn^{2+}(NH_3)}$ and $\mathrm{Cu^{2+}}$ (acetate buffer, pH 5·2).

Subjects not much studied are the development of suitable indicators for the complexometric titrations of transition metals, *e.g.*, by introducing chromophoric and hydrophilic groups into the dioxime molecule, and the preparation of ion-specific electrodes, especially for the nickel ion. It does not seem possible to prepare a good electrode from nickel dimethylglyoximate.[216]

A somewhat unusual dioxime, biacetyloximeazine [C(NOH)—C=N—N=C—C(NOH)] has been synthesized because of its structural relationship with dimethylglyoxime.[217] The complex formed with nickel is slightly soluble in water. The complex molecule in the solid state is a dimer consisting of two nickel atoms and two oximeazine molecules. No hydrogen bonds are formed between the oxime groups of the two ligands. The nickel ions may be more exchangeable than in nickel dimethylglyoximate and the complex may be useful for the preparation of a nickel-selective electrode. Many unusual dioximes have been prepared as model substances for the study of biochemical (enzymatic) processes. This is only one aspect of the co-ordination chemistry of dioximes; the analytical application of such investigations will, however, probably be of minor importance.

Acknowledgement—Very grateful acknowledgement is due to Professor David Dyrssen for helpful discussions of this review and the material presented in it.

Zusammenfassung—Es wird eine Übersicht über die Chemie und analytische Anwendungen von Metall-Dioximkomplexen gegeben.

Résumé—On présente une revue sur la chimie et les applications analytiques des complexes de dioxime avec les métaux.

REFERENCES

1. L. Z. Tschugaeff, *Z. Anorg. Allgem. Chem.*, 1905, **46**, 144.
2. D. Dyrssen, *Trans. Roy. Inst. Technol., Stockholm*, 1964, 220.
3. E. Uhlig and E. Mann, *Z. Anorg. Allgem. Chem.*, 1963, **325**, 209.
4. L. S. Bark and D. Brandon, *Talanta*, 1969, **16**, 497.
5. J. Basset, G. B. Leton and A. I. Vogel, *Analyst*, 1967, **92**, 279.
6. G. St. Nikolov and N. Tyutyulkov, *Inorg. Nucl. Chem. Letters*, 1970, **6**, 697.
7. A. K. Babko, *Nauk Zapiski Kievsk, Univ. im. T. G. Shevchenka.*, 1956, 241.
8. C. V. Banks, *Analytical Chemistry 1962*, Proc. *Intern. Symp., Birmingham, 1962*, Ed. Ph. W. West, A. M. G. Macdonald, and T. S. West, p. 131. Elsevier, Amsterdam, 1963.
9. C. V. Banks, 16th Annual Summer Symposium on Analytical Chemistry, Tucson, U.S.A. 19–21 June 1963.
10. C. V. Banks, *Rec. Chem. Prog.*, 1964, **25**, 85.
11. D. Dyrssen, *Svensk Kem. Tidskr.*, 1963, **75**, 618.
12. K. Burger, in H. A. Flaschka and A. J. Barnard, Jr., *Chelates in Analytical Chemistry*, Vol. II, p. 179. Dekker, New York, 1969.
13. D. Monnier and W. Haerdi, *Helv. Chim. Acta*, 1958, **41**, 2205.
14. J. Toul, J. Padrta and A. Okáč, *J. Chromatog.*, 1971, **57**, 107.
15. H. E. Ungnade, G. Fritz and L. W. Kissinger, *Tetrahedron*, 1963, **19**, Suppl. 1, 235.
16. J. V. Burakevich, A. M. Lore and G. P. Volpp, *J. Org. Chem.*, 1971, **36**, 1.
17. K. Shinra and K. Ishikawa, *Nippon Kagaku Zasshi*, 1953, **74**, 271.
18. K. Yamasaki and T. Matsumoto, *ibid.*, 1955, **76**, 569.
19. K. Yamasaki, T. Matsumoto and R. Ito, *ibid.*, 1957, **78**, 126.
20. G. G. Kleinspehn, J. A. Jung and S. A. Studniarz, *J. Org. Chem.*, 1967, **32**, 460.
21. J.-P. Guetté, J. Armand and L. Lacombe, *Compt. Rend. Ser. C*, 1967, **264**, 1509.
22. M. Tanaka, T. Shono and K. Shinra, *Anal. Chim. Acta*, 1969, **46**, 125.
23. M. Calleri, G. Ferraris and D. Viterbo, *Acta Cryst.*, 1966, **20**, 73.
24. L. L. Merrit, Jr. and E. Lanterman, *ibid.*, 1952, **5**, 811.
25. W. C. Hamilton, *ibid.*, 1961, **14**, 95.
26. C. Pigenet, J. Armand and H. Lumbroso, *Bull. Soc. Chim. France*, 1970, 2124.
27. E. Borello and M. Colombo, *Gazz. Chim. Ital.*, 1957, **87**, 615.
28. B. Roos, *Acta Chem. Scand.*, 1965, **19**, 1715.
29. M. Bossa and G. Morpurgo, *Ric. Sci.*, 1967, **37**, 1131.
30. B. Egneus, *Anal. Chim. Acta*, 1968, **43**, 53.
31. V. I. Shlenskaya, T. I. Tikhvinskaya and A. A. Biryukov, *Vestn. Mosk. Univ. Ser. II, Khim.*, 1970, 337.
32. P. R. Ellefsen and L. Gordon, *Talanta*, 1967, **14**, 409.
33. A. N. Alybina and V. M. Peshkova, *Vestn. Mosk. Univ. Ser. II, Khim*, 1970, 260.

34. M. Spritzer and L. Meites, *Anal. Chim. Acta*, 1962, **26**, 58.
35. K. Burger, G. Syrek and G. Farsang, *Acta Chim. Acad. Sci. Hung.*, 1966, **49**, 113.
36. A. Narayanan and P. R. Subbaraman, *Indian J. Chem.*, 1967, **5**, 153.
37. V. Bossa, G. Morpurgo and L. Morpurgo, *Ric. Sci.*, 1967, **37**, 402.
38. R. I. Gelb and L. Meites, *J. Phys. Chem.*, 1964, **68**, 2599.
39. E. O. Schlemper, *Inorg. Chem.*, 1969, **8**, 2740.
40. A. Vaciago and L. Zambonelli, *J. Chem. Soc.* (*A*), 1970, 218.
41. E. Frasson, R. Bardi and S. Bezzi, *Acta Cryst.*, 1959, **12**, 201.
42. D. H. Svedung, *Acta Chem. Scand.*, 1969, **23**, 2865.
43. C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, 1958, **80**, 3579.
44. L. E. Godycki and R. E. Rundle, *Acta Cryst.*, 1953, **6**, 487.
45. M. Calleri, G. Ferraris and D. Viterbo, *ibid.*, 1967, **22**, 468.
46. R. K. Murmann and E. O. Schlemper, *ibid.*, 1967, **23**, 667.
47. M. Calleri, G. Ferraris and D. Viterbo, *Inorg. Chim. Acta*, 1967, **1**, 297.
48. G. Ferraris and D. Viterbo, *Acta Cryst.*, 1969, **B25**, 2066.
49. B. G. Anex and F. K. Krist, *J. Am. Chem. Soc.*, 1967, **89**, 6114.
50. E. Frasson and C. Panattoni, *Acta Cryst.*, 1960, **13**, 893.
51. A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 1957, 281.
52. P. M. Zorkii, M. A. Porai-Koshits and V. S. Psalidas, *Zh. Strukt. Khim.*, 1966, **7**, 577.
53. L. F. Lindoy, S. E. Livingstone and N. C. Stephenson, *Inorg. Chim. Acta*, 1967, **1**, 161.
54. G. Basu, G. M. Cook and R. L. Belford, *Inorg. Chem.*, 1964, **3**, 1361.
55. K. Takiyama, Y. Tanigawa, Y. Yamada, T. Maehera, H. Sakashita, M. Mizukai and M. Tsubota, *Bunseki Kagaku*, 1970, **19**, 1264.
56. S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1954, **27**, 156.
57. C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, 1958, **80**, 4767.
58. Y. Ohashi, I. Hanazaki and S. Nagakura, *Inorg. Chem.*, 1970, **9**, 2551.
59. C. V. Banks and S. Andersson, *J. Am. Chem. Soc.*, 1962, **84**, 1486.
60. L. L. Ingraham, *Acta Chem. Scand.*, 1966, **20**, 283.
61. B. Roos, *ibid.*, 1967, **21**, 1855.
62. J. E. Caton, Jr. and C. V. Banks, *Talanta*, 1966, **13**, 967.
63. D. Dyrssen and D. Petkovíc, *Acta Chem. Scand.*, 1965, **19**, 653.
64. C. Matsumoto, Y. Yamano and K. Shinra, *Nippon Kagaku Zasshi*, 1968, **89**, 44.
65. A. K. Babko, P. B. Mikhel'son and S. A. Romanenko, *Zh. Neorgan. Khim.*, 1968, **13**, 731 (*Russ. J. Inorg. Chem.*, 1968, **13**, 382).
66. A. K. Babko, P. B. Mikehl'son, E. P. Lyubchik and P. S. Dzyuba, *ibid.*, 1969, **14**, 1302 (*Russ. J. Inorg. Chem.*, 1969, **14**, 681).
67. N. Sanders and P. Day, *J. Chem. Soc.* (*A*), 1969, 2303.
68. C. Matsumoto, T. Kato and K. Shinra, *Nippon Kagaku Zasshi*, 1965, **86**, 1266.
69. C. Matsumoto, I. Masuda and K. Shinra, *ibid.*, 1967, **88**, 46.
70. I. P. Alimarin, A. A. Biryukov, T. I. Tikvinskaja and V. I. Shlenskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1969, 45.
71. A. K. Babko, P. B. Mikhel'son, L. V. Karpova and N. N. Karpus, *Zh. Neorgan. Khim.*, 1969, **14**, 124 (*Russ. J. Inorg. Chem.*, 1969, **14**, 65).
72. V. H. Galgali, V. R. Rao and D. D. Khanolkar, *Indian J. Chem.*, 1969, **7**, 825.
73. R. Blinc and D. Hadži, *J. Chem. Soc.*, 1958, 4536.
74. K. Burger, I. Ruff and F. Ruff, *J. Inorg. Nucl. Chem.*, 1965, **27**, 179.
75. J. E. Caton, Jr. and C. V. Banks, *Inorg. Chem.*, 1967, **6**, 1670.
76. A. Bigotto, G. Costa, V. Galasso and G. De Alti, *Spectrochim. Acta*, 1970, **26A**, 1939.
77. A. Bigotto, V. Galasso and G. De Alti, *ibid.*, 1971, **27A**, 1659.
78. R. E. Rundle, *J. Phys.*, 1964, **25**, 487.
79. P. B. Mikhel'son and N. P. Evtushenko, *Zh. Neorgan. Khim.*, 1970, **15**, 1539, (Russ. J. Inorg. Chem., 1970, **15**, 790).
80. W. Schübel and E. Lutze, *Z. Angew. Phys.*, 1964, **17**, 332.
81. K.-E. Falk, E. Ivanova, B. Roos and T. Vänngård, *Inorg. Chem.*, 1970, **9**, 556.
82. D. Dyrssen and M. Hennichs, *Acta Chem. Scand.*, 1961, **15**, 47.
83. D. Dyrssen, K.-E. Falk and E. K. Ivanova, *Acta Chem. Scand.*, in the press.
84. I. N. Marov, E. S. Gur'eva and V. M. Peshkova, *Zh. Neorgan. Khim.*, 1970, **15**, 3039 (*Russ. J. Inorg. Chem.*, 1970, **15**, 1583).
85. H. A. O. Hill and K. G. Morallee, *J. Chem. Soc.* (*A*), 1969, 554.
86. M. Naumberg, K. N. van Duong, F. Gaudemer and A. Gaudemer, *Compt. Rend. Ser. C*, 1970, **270**, 1301.
87. K. Burger, L. Korecz, I. B. A. Manuaba and P. Mag, *J. Inorg. Nucl. Chem.*, 1966, **28**, 1673.
88. K. Burger and E. Papp-Molnár, *Acta Chim. Acad. Sci. Hung.*, 1967, **53**, 111.

89. J. L. K. F. de Vries, J. M. Trooster and E. de Boer, *J. Chem. Soc. (D)*, 1970, 604.
90. A. V. Ablov, V. I. Gol'danskii, R. A. Stukan and E. F. Makarov, *Dokl. Akad. Nauk SSSR*, 1966, **170**, 128.
91. Yu. A. Zolotov and G. E. Vlasova, *Zh. Analit. Khim.*, 1969, **24**, 1542.
92. G. P. Syrtsova and N. Z. Lyong, *Zh. Neorgan. Khim.*, 1970, **15**, 1027 (*Russ. J. Inorg. Chem.*, 1970, **15**, 523).
93. A. V. Ablov, N. M. Samus and O. A. Bologa, *ibid.*, 1963, **8**, 860 (*Russ. J. Inorg. Chem.*, 1963, **8**, 440).
94. A. V. Ablov, O. A. Bologa and N. M. Samus', *ibid.*, 1968, **13**, 3269 (*Russ. J. Inorg. Chem.*, 1968, **13**, 1685).
95. Z. Finta, J. Zsako and Cs. Várhelyi, *Z. Phys. Chem.*, 1969, **242**, 200.
96. T. I. Malinoskii, Yu. A. Simonov and B. M. Shchedrin, *Kristallografiya*, 1969, **14**, 995.
97. A. V. Ablov and G. P. Syrtsova, *Zh. Neorgan. Khim.*, 1965, **10**, 1980 (*Russ. J. Inorg. Chem.*, 1965, **10**, 1079).
98. N. Maki, *Bull. Chem. Soc. Japan*, 1965, **38**, 2013.
99. N. Maki and S. Sakuraba, *ibid.*, 1969, **42**, 1908.
100. A. V. Ablov, N. M. Samus' and A. A. Popova, *Zh. Neorgan. Khim.*, 1971, **16**, 411 (*Russ. J. Inorg. Chem.*, 1971, **16**, 215).
101. Cs. Várhelyi, J. Zsakó and Z. Finta, *Monatsheft.* 1970, **101**, 1013.
102. A. V. Ablov, D. G. Batyr and M. P. Starysh, *Zh. Neorgan. Khim.*, 1970, **15**, 1713 (*Russ. J. Inorg. Chem.*, 1970, **15**, 880).
103. Cs. Várhelyi and B. Bohm, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 1964, **9**, 55.
104. R. Ripan, Cs. Várhelyi and E. Libal, *ibid.*, 1965, **10**, 33.
105. A. V. Ablov, B. A. Bovykin and N. M. Samus, *Dokl. Akad. Nauk SSSR*, 1965, **163**, 635.
106. A. Soo, C. Várhelyi and A. Sipos, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 1968, **13**, 79.
107. R. Ripan, Cs. Várhelyi and E. Kekedy, *ibid.*, 1965, **10**, 19.
108. A. V. Ablov, D. G. Batyr and M. P. Starysh, *Zh. Neorgan. Khim.*, 1971, **16**, 690 (*Russ. J. Inorg. Chem.*, 1971, **16**, 368).
109. V. N. Evreev, V. A. Golub and S. V. Murashko, *ibid.*, 1971, **16**, 716 (*Russ. J. Inorg. Chem.*, 1971, **16**, 382).
110. N. N. Proskina, A. V. Ablov and V. N. Shafranskii, *ibid.*, 1969, **14**, 3034 (*Russ. J. Inorg. Chem.*, 1969, **14**, 1599).
111. A. V. Ablov, N. N. Proskina and Ch'ang T'hi Tam Tang, *ibid.*, 1971, **16**, 699 (*Russ. J. Inorg. Chem.*, 1971, **16**, 373).
112. Cs. Várhelyi, Z. Finta and J. Zsakó, *Z. Anorg. Allgem. Chem.*, 1970, **374**, 326.
113. Cs. Várhelyi and L. Szotyori, *Rev. Roum. Chim.*, 1965, **10**, 1049.
114. O. G. Mikhailova and I. P. Ryazanov, *Izv. Vyssh. Ucheb. Zaved., Khim. i Khim. Tekhnol.*, 1970, **13**, 1393.
115. Cs. Várhelyi, L. Szotyori and I. Edler, *Rev. Roum. Chim.*, 1966, **11**, 497.
116. N. Z. Lyong and G. P. Syrtsova, *Zh. Neorgan. Khim.*, 1971, **16**, 704 (*Russ. J. Inorg. Chem.*, 1971, **16**, 376).
117. R. Ripan, Cs. Várhelyi and L. Szotyori, *Stud. Univ. Babes-Balyai, Ser. Chem.*, 1967, **12**, 133.
118. *Idem*, *Z. Anorg. Allgem. Chem.*, 1968, **357**, 149.
119. R. Spacu, M. Brezeanu and D. Roman-Vacarescu, *An. Univ. Bucaresti, Ser. Stiint. Nat.*, 1963, **12**, 63.
120. A. V. Ablov, N. M. Samus' and O. A. Bologa, *Zh. Neorgan. Khim.*, 1969, **14**, 3320 (*Russ. J. Inorg. Chem.*, 1969, **14**, 1751).
121. G. P. Syrtsova, *ibid.*, 1970, **15**, 1308 (*Russ. J. Inorg. Chem.*, 1970, **15**, 671).
122. R. Ripan, Cs. Várhelyi and R. Boehm, *Stud. Univ. Babes-Bolyai, Ser. Chem.*, 1965, **10**, 87.
123. V. Borodulina-shvet, I. P. Rudakova and S. F. Dymvoa, *Zh. Obshch. Khim.*, 1970, **40**, 703.
124. A. V. Ablov, B. A. Bovykin and N. M. Samus', *Zh. Neorgan. Khim.*, 1966, **11**, 1832 (*Russ. J. Inorg. Chem.*, 1966, **11**, 978).
125. D. M. Palade, T. N. Volokh, N. A. Breslavskaya and T. N. Golyshina, *ibid.*, 1970, **15**, 2698 (*Russ. J. Inorg. Chem.*, 1970, **15**, 1401).
126. J. P. Birk, P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, 1968, **90**, 6959.
127. Y. Yamano, I. Masuda and K. Shinra, *Inorg. Nucl. Chem. Letters*, 1968, **4**, 581.
128. I. Masuda, M. Sakano and K. Shinra, *Bull. Chem. Soc. Japan*, 1969, **42**, 2296.
129. V. I. Dubinskii, *Zh. Neorgan. Khim.*, 1971, **16**, 696 (*Russ. J. Inorg. Chem.*, 1971, **16**, 371).
130. K. Burger, B. Zelei, G. Szántho-Horváth and T. T. Binh, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2573.
131. G. P. Syrtsova and T. S. Bolgar, *Zh. Neorgan. Khim.*, 1969, **14**, 2425 (*Russ. J. Inorg. Chem.* 1969, **14**, 1272).
132. *Idem*, *ibid.*, 1970, **15**, 1714 (*Russ. J. Inorg. Chem.*, 1970, **15**, 881).

133. P. Powell, *J. Chem. Soc. A*, 1969, 2418.
134. K. Burger, I. Ruff and F. Ruff, *Magy. Kem. Folyoirat*, 1964, **70**, 394.
135. K. Burger and B. Pintér, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1717.
136. K. Burger and I. Ruff, *Acta Chim. Acad. Sci. Hung.*, 1964, **41**, 75.
137. K. Burger, B. Pintér, E. Papp-Molnár and S. Nemes-Kósa, *ibid.*, 1968, **57**, 363.
138. G. C. S. Manku, *Z. Anorg. Allgem. Chem.*, 1971, **382**, 202.
139. V. M. Savostina, E. K. Astakhova and V. M. Peshkova, *Vestn. Mosk. Univ. Ser. II, Khim.*, 1963, **18**, 43.
140. *Idem, Zh. Neorgan. Khim.*, 1964, **9**, 80 (*Russ. J. Inorg. Chem.*, 1964, **9**, 42).
141. E. K. Astakhova, V. M. Savostina and V. M. Peshkova, *ibid.*, 1964, **9**, 817 (*Russ. J. Inorg. Chem.*, 1964, **9**, 452).
142. A. A. Biryukov, V. I. Shlenskaya, I. P. Alimarin and T. I. Tikvinskaya, *ibid.*, 1966, **11**, 1679 (*Russ. J. Inorg. Chem.*, 1966, **11**, 897).
143. P. B. Mikhel'son and L. V. Kalabina, *Zh. Analit. Khim.*, 1969, **24**, 261.
144. B. Egneus, *Anal. Chim. Acta*, 1969, **48**, 291.
145. R. Días Cadavieco, M. P. C. de Días, D. Dyrssen and B. Egneus, *Trans. Roy. Inst. Technol., Stockholm*, in the press.
146. A. N. Alybina, E. K. Ivanova and V. M. Peshkova, *Vestn. Mosk. Univ. Ser. II, Khim.*, 1969, 93.
147. V. I. Shlenskaya, T. I. Tikvinskaya, A. A. Biryukov and I. P. Alimarin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, 2141.
148. F. Manok, Cs. Várhelyi and S. Kiss-Rajhona, *Rev. Roum. Chim.*, 1969, **14**, 1251.
149. E. K. Astakhova, V. M. Savostina and V. M. Peshkova, *Zh. Fiz. Khim.*, 1964, **38**, 2299.
150. V. Peshkova, V. Savostina and E. Astakhova-Ivanova, in *Solvent Extraction Chemistry*, Proc. Intern. Conf., Gothenburg, Sweden, 27 August–1 September 1966, (Ed. D. Dyrssen, J.-O. Liljenzin and J. Rydberg), p. 66. North-Holland, Amsterdam, 1967.
151. I. P. Alimarin, T. I. Tikhvinskaya, V. I. Shlenskaya and A. S. Biryukov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 2675.
152. P. B. Mikhel'son and V. I. Kozachek, *Zh. Analit. Khim.*, 1966, **21**, 1255.
153. V. M. Peshkova, V. M. Savostina, E. K. Astakhova and N. A. Minaeva, *Tr. Komis. po Analit. Khim. Akad. Nauk SSSR, Inst. Geokhim. i Analit. Khim.*, 1965, **15**, 104.
154. T. I. Tikvinskaya, A. A. Biryukov, V. I. Shlenskaya and N. K. Gordynskaya, *Zh. Neorgan. Khim.*, 1970, **15**, 128 (*Russ. J. Inorg. Chem.*, 1970, **15**, 65).
155. H. Einaga and H. Ishii, *Bull. Chem. Soc. Japan*, 1970, **43**, 2970.
156. G. Liptay, E. Papp-Molnár and K. Burger, *J. Inorg. Nucl. Chem.*, 1969, **31**, 247.
157. K. Burger and D. Dyrssen, *Acta Chem. Scand.*, 1963, **17**, 1489.
158. R. L. Motley and C. E. Meloan, *Sep. Sci.*, 1968, **3**, 279.
159. P. B. Mikhel'son, A. K. Boryak and L. T. Moshkovskaya, *Zh. Analit. Khim.*, 1971, **26**, 787.
160. E. D. Salesin and L. Gordon, *Talanta*, 1960, **5**, 81.
161. K. Takyiama and L. Gordon, *ibid*, 1963, **10**, 1165.
162. R. J. Magee and L. Gordon, *Proc. SAC Conf. Nottingham, 1965* (Ed. P. W. Shallis) p. 378 Heffer, Cambridge, 1965.
163. E. D. Salesin, E. W. Abrahamson and L. Gordon, *Talanta*, 1962, **9**, 699.
164. M. A. Bambenek and R. T. Pflaum, *Inorg. Chem.*, 1963, **2**, 289.
165. A. P. Rollet, *Compt. Rend. Ser. C.*, 1926, **183**, 212.
166. D. J. Davis and E. A. Boudreaux, *J. Electroanal. Chem.*, 1964, **8**, 434.
167. M. K. Boreiko and I. I. Kalinichenko, *Zh. Analit. Khim.*, 1968, **23**, 1662.
168. I. I. Kalinichenko and M. K. Boreiko, *Zh. Neorgan. Khim.*, 1969, **14**, 766 (*Russ. J. Inorg. Chem.*, 1969, **14**, 401).
169. M. K. Boreiko, E. I. Kazantsev and I. I. Kalinichenko, *ibid.*, 1967, **12**, 269 (*Russ. J. Inorg. Chem.*, 1967, **12**, 522).
170. M. K. Boreiko and I. I. Kalinichenko, *Zh. Analit. Khim.*, 1968, **23**, 1359.
171. O. S. Ksenzhek, L. S. Burachenko, I. O. Volodina, F. E. Dinkevich and G. G. Motyagina, *Zh. Neorgan. Khim.*, 1971, **16**, 1064 (*Russ. J. Inorg. Chem.*, 1971, **16**, 566).
172. L. Brady and M. Muers, *J. Chem. Soc.*, 1930, 1599.
173. D. Fleischer and H. Freiser, *J. Phys. Chem.*, 1962, **66**, 389.
174. E. Uhlig and D. Dorn, *Z. Chem.*, 1971, **11**, 187.
175. K. Kodama and N. Kodama, *Nagyoyashi Kogya Kenkyusho Kenkyu, Hokoku*, 1966, **35**, 1; *Chem. Abstr.*, 1968, **69**, 48971u.
176. E. N. Pollock and L. P. Zopatti, *Anal. Chim. Acta*, 1965, **32**, 418.
177. H.-G. Döge and H. Grose-Ruyken, *Mikrochim. Acta*, 1967, 98.
178. M. Kozlicka, M. Wojtowicz and I. Adamiec *Chem. Anal.* (*Warsaw*), 1970, **15**, 701.
179. G. V. Nikolaevna and I. A. Stolyarova, *Tr. Vses. Nauchn.-Issled. Geol. Inst.*, 1964, **117**, 89.
180. K. S. Bergstresser, *U.S. At. Energy Comm. Rept.*, LA-3213, 1965.

181. J. C. Muller and C. Ferradini, *Radiochem. Radioanal. Lett.*, 1969, **2**, 273.
182. N. Masuda and M. Kajiwara, *Bunseki Kagaku*, 1968, **17**, 1353.
183. *Idem, ibid.*, 1970, **19**, 1613.
184. K. Burger and I. Ruff, *Acta Chim. Acad. Sci. Hung.*, 1965, **45**, 77.
185. J. L. Jones and J. Gastfield, *Anal. Chim. Acta*, 1970, **51**, 130.
186. S. J. Lyle and R. Maghzian, *Talanta*, 1969, **16**, 1535.
187. E. Kentner, D. B. Armitage and H. Zeitlin, *Anal. Chim. Acta*, 1969, **43**, 343.
188. T. E. Green, *Anal. Chem.*, 1965, **37**, 1595.
189. L. Gordon, P. R. Ellefsen, G. Wood and O. E. Hileman, Jr., *Talanta*, 1966, **13**, 551.
190. S. J. Lyle and R. Maghzian, *ibid.*, 1967, **14**, 1021.
191. A. Claassen and L. Bastings, *Analyst*, 1966, **91**, 725.
192. K. Izutsu, Y. Tanigawa and K. Takiyama, *Talanta*, 1965, **12**, 179.
193. V. Ya. Doroshkov and V. T. Cheriko, *Khim. Tekhn.*, 1968, No. 13, 69.
194. M. V. Korothun, *Izv. Vyssh. Ucheb. Zaved., Khim. i Khim. Tekhn.*, 1969, **12**, 1296.
195. P. Luis and C. N. Carducci, *Microchim. Acta*, 1971, 124.
196. A. E. Jenkins and J. R. Majer, *Talanta*, 1967, **14**, 777.
197. M. M. Barling and Ch. V. Banks, *Anal. Chem.*, 1964, **36**, 2359.
198. V. M. Peshkova, E. K. Astakhova, I. F. Dolmanova and V. M. Savostina, *Acta Chim. Acad. Sci. Hung.*, 1967, **53**, 121.
199. V. M. Peshkova and N. G. Ignat'eva, *Zh. Analit. Khim.*, 1962, **17**, 1086.
200. D. E. Bodart, *Z. Anal. Chem.*, 1969, **247**, 32.
201. A. L. Wilson, *Proc. SAC Conf., Nottingham, 1965* (Ed. P. W. Shallis) p. 361. Heffer, Cambridge, 1965.
202. K. S. Pakhomova, L. P. Volkova and V. V. Gorshov, *Zh. Analit. Khim.*, 1964, **19**, 1085.
203. G. H. Ayres and J. B. Martin, *Anal. Chim. Acta*, 1966, **35**, 181.
204. Z. Marczenko, *Chim. Anal. (Paris)*, 1964, **46**, 286.
205. Z. Marczenko and M. Krasiejko, *Chem. Anal. (Warsaw)*, 1964, **9**, 291.
206. J. A. Velazquez and O. E. Hileman, Jr., *Talanta*, 1968, **15**, 269.
207. O. M. Ivonina, *Zh. Analit. Khim.*, 1964, **19**, 644.
208. Z. Gregorowicz, F. Buhl and Z. Klima, *Chem. Anal. (Warsaw)*, 1965, **10**, 1043.
209. V. I. Kuznetsov and V. A. Marugin, *Zavodsk. Lab.*, 1970, **36**, 1318.
210. N. V. Benediktova-Lodochnikova, *Zh. Analit. Khim.*, 1963, **18**, 1322.
211. E. B. Sandell, *Colorimetric Determination of Traces of Metals, 3rd Ed.*, p. 668. Interscience, New York, 1959.
212. R. A. Blomfield, J. C. Guyon and R. K. Murmann, *Anal. Chem.*, 1965, **37**, 248.
213. N. M. Petrun and N. K. Litvinchuk, *Lab. Delo*, 1969, 414.
214. V. A. Khramov and N. J. Narbutovich, *ibid.*, 1969, 439.
215. W. Szczepaniak and G. Kubera, *Chem. Anal. (Warsaw)*, 1970, **15**, 1009.
216. S. Morazzani-Pelletier and M. A. Baffier, *J. Chim. Phys.*, 1965, **62**, 429.
217. W. J. Stratton and P. J. Ogren, *Inorg. Chem.*, 1970, **9**, 2588.

Talanta, 1972, Vol. 19, pp. 1421 to 1427. Pergamon Press. Printed in Northern Ireland

NEW MASKING PROCEDURE FOR SELECTIVE COMPLEXOMETRIC DETERMINATION OF COPPER(II)

RAJINDER PAL SINGH
Department of Chemistry, Panjabi University, Patiala, India

(*Received* 22 *March* 1971. *Revised* 14 *April* 1972. *Accepted* 23 *April* 1972)

Summary—A study has been made of a new masking procedure for highly selective complexometric determination of copper(II), based on decomposition of the copper–EDTA complex at pH 5–6. Among the various combinations of masking agents tried, ternary masking mixtures comprising a main complexing agent (thiourea), a reducing agent (ascorbic acid) and an auxiliary complexing agent (thiosemicarbazide or a small amount of 1,10-phenanthroline or 2,2′-dipyridyl) have been found most suitable. An excess of EDTA is added and the surplus EDTA is back-titrated with lead (or zinc) nitrate with Xylenol Orange as indicator (pH 5–6). A masking mixture is then added to decompose the copper–EDTA complex and the liberated EDTA is again back-titrated with lead (or zinc) nitrate. The following cations do not interfere: Ag^+, Hg^{2+}, Pb^{2+}, Ni^{2+}, Bi^{3+}, As^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+}, Cd^{2+}, Co^{2+}, Cr^{3+} and moderate amounts of Fe^{3+} and Mn^{2+}. The notable feature is that consecutive determination of Hg^{2+} and Cu^{2+} can be conveniently carried out in the presence of other cations.

As the direct complexometric methods for the determination of copper are not selective it is usually determined in the presence of some other cations by performing two separate titrations. The sum of all the cations including copper is first determined by back-titration of a known excess of EDTA with lead nitrate, with Xylenol Orange as indicator (pH 5–6), then in the second aliquot copper is masked by thiourea and the sum of the remaining cations is determined by a similar titration. The difference in the two titration results corresponds to copper.

A convenient method of determining copper selectively however, is to decompose the copper–EDTA complex (I) with a suitable masking agent and determine the liberated EDTA by back-titration. Only a few masking agents have been proposed for this purpose, which decompose I by displacement. 1,10-Phenanthroline[1] in acidic medium and thioglycollic acid[2] in alkaline medium have been used but both lack selectivity. Cystein[3] has also been proposed as the masking agent but cadmium, bismuth and mercury interfere. Budevsky and Simova[4] have recommended the use of thiourea in strongly acidified solution for masking but as the EDTA complexes of other bivalent metals also decompose at this low pH, the method suffers from the serious interference of cadmium, mercury, manganese and cobalt. The method is also time-consuming and inconvenient.

The present study was undertaken to develop a convenient masking procedure for fast and selective decomposition of I at the pH (5–6) at which the back-titration with lead (or zinc) nitrate is carried out with Xylenol Orange as indicator. Obviously more selective masking would be obtained by reduction of I to yield copper(I) and complexation of that with a masking agent such as thiourea or sodium thiosulphate. This, however, presents a difficult problem as these masking agents have little effect on I at pH 5–6, first because of the lowering of the redox potential[5] of the Cu^{2+}/Cu^+

system and secondly, and more importantly, because the copper(II) is surrounded by a large saturated ligand and electron transfer is sluggish. A detailed study was therefore undertaken, in which common masking agents were tried in various combinations to decompose **I** (Table I). It was found that although certain binary mixtures give quite satisfactory results, fast and smooth decomposition is best brought about by ternary mixtures. Each mixture, in general, comprises an auxiliary complexing agent (a small amount of 1,10-phenanthroline or 2,2′-dipyridyl and thiosemicarbazide), a reducing agent (ascorbic acid) and the main complexing agent (thiourea, sodium thiosulphate or thiosemicarbazide).

TABLE I.—EFFECT OF VARIOUS MASKING AGENTS ON THE DECOMPOSITION OF COPPER-EDTA COMPLEX (at pH 5–5·5).

Masking agent(s)*	Decomposition
TU, hypo	Almost nil
AA	Slight
TU, hypo + AA	Slight
TSC	Incomplete
TSC + AA	Incomplete
TSC + AA + phen (dipy)	Incomplete
TU + TSC	Complete†
TU + TSC + phen (dipy)	Complete†
TU + AA + TSC	Complete, fast
Hypo + TSC	Complete, slow
Hypo + TSC + phen (dipy)	Complete, slow
Hypo + AA + TSC	Complete, fast
Hypo + AA + phen (dipy)	Incomplete
TU + AA + phen (dipy)	Complete, fast

* TU = thiourea; hypo = sodium thiosulphate; AA = ascorbic acid; TSC = thiosemicarbazide; phen = 1,10-phenanthroline (small amount); dipy = 2,2′-dipyridyl (small amount).

† Slightly slow near the end-point.

On the basis of experimental findings and the stability constants[6] of the various complexes involved, the catalytic effect of a small amount of 2,2′-dipyridyl or (1,10-phenanthroline) on the masking of **I** in the presence of a mixture of thiourea and ascorbic acid can be explained as follows.

A small amount of copper(II) is withdrawn from **I** by the auxiliary masking agents as these form stronger complexes with it.

$$CuY^{2-} + 3\ dipy = Cu(dipy)_3^{2+} + Y^{4-} \qquad (1)$$

$$(\log K = 12{\cdot}2) \qquad (\log K = 17{\cdot}85)$$

As the copper ion is now surrounded by a large unsaturated ligand instead of the saturated EDTA ligand the exchange of electrons can be much faster.[7] The new complex is, therefore, readily reduced by ascorbic acid to the corresponding copper(I) complex.

$$Cu(dipy)_3^{2+} + e = Cu(dipy)_2^{+} + dipy \qquad (2)$$

As thiourea forms a more stable complex with copper(I) the auxiliary complexing agent is finally liberated from its copper(I) complex by the excess of thiourea

$$Cu(dipy)_2^{+} + 4\ tu = Cu(tu)_4^{+} + 2\ dipy \qquad (3)$$

$$(\log K = 14{\cdot}2) \qquad (\log K = 15{\cdot}4)$$

and is thus made available for further decomposition of **I**. In this three-stage process each stage is brought about by an individual constituent of the masking mixture, the cumulative effect of which leads to the fast and complete decomposition of **I**. When sodium thiosulphate and thiosemicarbazide are used in the masking mixture in place of thiourea, the addition of the auxiliary masking agents (1,10-phenanthroline or 2,2′-dipyridyl) does not enhance the speed of decomposition of **I**, because the thiosulphate and thiosemicarbazide complexes of copper(I) are too weak ($\log K = 13{\cdot}8$ and $11{\cdot}2$ respectively) to liberate the auxiliary masking agent by the displacement reaction (3). The presence of ascorbic acid in the masking mixture is essential as the redox potential of the Cu^{2+}/Cu^{+} system, although favourably affected by the presence of auxiliary complexing agent,[8] is nevertheless apparently not sufficiently high to enable thiourea alone to bring about the reduction [equation (2)].

As thiosemicarbazide is an important constituent of some masking mixtures, it was considered necessary to study its role in the masking of free copper(II). In the literature[9] thiosemicarbazide has been recommended for the masking of mercury and mercury–EDTA complex only, and copper(II) has been found to interfere seriously by forming an intense blue colour. In the course of the present study it was noted that the blue complex $Cu(TSC)_2^{2+}$ which is formed at low pH undergoes partial self-reduction slowly as the pH is raised to 5–6. This reduction to colourless $Cu(TSC)_2^{+}$ is made instantaneous by the addition of ascorbic acid. Thus this mixture can be conveniently used for masking of free copper(II) at pH 5–6. The masking of **I** by ternary masking mixtures with thiosemicarbazide as a constituent is thus also a three-stage process as described above. Here thiosemicarbazide behaves similarly to 2,2′-dipyridyl or 1,10-phenanthroline, the only difference being that the amount required is comparatively larger, although much smaller than required in binary mixtures for masking free copper(II). Unlike the ternary mixture with 1,10-phenanthroline or 2,2′-dipyridyl the presence of ascorbic acid in this masking mixture is not necessary, because reduction is facilitated by thiourea itself. In the binary mixtures of thiosemicarbazide and ascorbic acid the former has a dual function in the first and the third stage of the masking.

EXPERIMENTAL

Reagents

EDTA, 0·05M. Standardized against pure zinc, with Eriochrome Black T as indicator.

Copper nitrate 0·05M. Prepared from analytical grade copper metal.

Lead nitrate and zinc nitrate, 0·05M. Prepared from reagent grade salts and standardized with 0·05*M* EDTA, Xylenol Orange being used as indicator.

Xylenol Orange. Aqueous solution, 0·1%.

Thiourea and sodium thiosulphate. Aqueous solution, 1%.

Ascorbic acid. Aqueous solution, 5%.

1,10-*Phenanthroline and 2,2′-dipyridyl,* 0·1%. Prepared by dissolving the compounds in a little ethanol followed by dilution with demineralized water.

Potassium fluoride. Aqueous solution, 20%.

Hexamine. Reagent grade nitrates of the cations were used for studying interferences.

Determination of copper in the presence of other cations

To an acidic aliquot of the sample solution containing not more than 30 mg of copper, add excess of 0·05*M* EDTA, dilute the solution to about 50–100 ml with demineralized water and adjust the solution to pH 5–5·5 with solid hexamine. Add sufficient Xylenol Orange indicator and back-titrate the excess of EDTA with 0·05*M* lead (or zinc) nitrate to a sharp colour change from green-yellow to violet-blue or red-violet. Add 10 ml of 10% thiourea, about 5 ml of 5% ascorbic acid and 5 ml of 10% thiosemicarbazide for each 12 mg of copper, or 4–5 drops of 0·1% 1,0-phenanthroline (or 2,2′-dipyridyl) irrespective of the amount of copper. Shake till the solution becomes yellow and back-titrate the liberated EDTA with 0·05*M* lead (or zinc) nitrate to a sharp colour change from yellow to red-violet. Adjust the pH to 5–6 near the end-point, if necessary.

RESULTS AND DISCUSSION

Determinations of copper(II) were made with use of five different masking mixtures comprising thiourea, ascorbic acid and thiosemicarbazide; thiourea, ascorbic acid and 1,10-phenanthroline; thiourea, ascorbic acid and 2,2′-dipyridyl; sodium thiosulphate, ascorbic acid and thiosemicarbazide; and a mixture of thiourea and thiosemicarbazide. On the basis of detailed study the minimum amounts of the various constituents of these masking mixtures for the determination of 12 mg of copper were found to be 4–5 ml of 1% thiosemicarbazide solution, 8–10 ml of 10% thiourea solution, 10 ml of 10% sodium thiosulphate solution and 4–5 ml of 5% ascorbic acid solution, whereas 4–5 drops of 0·1% 1,10-phenanthroline or 2,2′-dipyridyl solution were found sufficient to catalyse the masking irrespective of the amount of copper determined. These amounts of a constituent may be varied slightly if larger amounts of the other constituents of the mixture are taken. When the binary mixture of thiourea and thiosemicarbazide is used, the amount of thiourea should be larger than normally required in the ternary mixture. Larger amounts of the masking agents do not affect the accuracy of the results. Although the order of addition of the masking agents does not appear to effect the speed of the masking process, in general thiourea was added first followed by ascorbic acid and 1,10-phenanthroline (or 2,2′-dipyridyl or thiosemicarbazide). As the constituents of the masking mixtures reinforce each other's effect on the decomposition of I they should be added at the beginning of the titration; their addition in lots during the course of the titration slightly slows down the masking.

Both lead and zinc nitrate can be used as back-titrants when thiosemicarbazide is used as one of the constituents of the masking mixture. In the masking catalysed by 1,10-phenanthroline or 2,2′-dipyridyl lead nitrate is somewhat more suitable as back-titrant; with zinc nitrate the results are slightly higher and the end-point is sharp only at pH 5·5–6. With the masking mixture containing sodium thiosulphate, only zinc nitrate should be used as the back-titrant and the pH at the end-point should preferably be between 5·5 and 6·0 for a sharp end-point.

The rate of masking is affected by the pH of the solution; lower pH makes the masking process faster. It is, therefore, preferable to carry out the masking at about pH 5 and adjust the solution to pH 5–6, if necessary, near the end-point. At the upper limit of the pH range the masking is somewhat slow but it is completed in the normal course of the titration (about 2 min). Accurate results are obtained with all the masking mixtures, and therefore the results are not given in separate tables.

Temperature has no appreciable effect on the rate of masking, and the titrations can be done at 15–35°. Too high a temperature makes the solution slightly turbid.

Interferences

Although Ag^+ is readily reduced to the metal by ascorbic acid and forms interfering precipitates with thiosemicarbazide, no interference is encountered if thiourea is added before the other consitiuents of the masking mixtures; transitory white precipitates are formed which dissolve on the addition of excess of thiourea to form a stable, soluble and colourless complex. Even large quantities of silver have no effect on the titration.

Zn^{2+}, Pb^{2+}, Ni^{2+}, As^{3+}, Sb^{3+} and Bi^{3+} do not interfere. Al^{3+} does not interfere at room temperature. Cd^{2+} and moderate amounts of Co^{2+} can be tolerated, but large amounts affect the quality of the end-point in the second back-titration. Zn^{2+} is a better back-titrant with larger amounts of Cd^{2+}. Large amounts of Cr^{3+} can also be tolerated. A small excess of EDTA should be added before the first back-titration otherwise the results are slightly high. As Mn^{2+} is only partially complexed at the pH used it tends to affect badly the sharpness of the end-point. Up to 10 mg of Mn^{2+} can easily be tolerated by maintaining the pH at the end-point at about 6 in both back-titrations. Tin, when present, can easily be removed as tin(IV) oxide by boiling with nitric acid.

As mercury(II) and mercury-EDTA complex are also masked readily by the masking agents used for masking copper(II) or **I**, they provide main interference in the determination of copper. A notable feature of the present method is that not only

TABLE II.—CATION INTERFERENCE STUDY IN THE DETERMINATION OF COPPER (13·5 mg). (EXPECTED VOLUME OF 0·05*M* EDTA LIBERATED = 4·25 ml).

Ion(s) added, *mg*	0·05*M* EDTA liberated, *ml*
—	4·25
—	4·26[a]
Ag$^+$ 107	4·25
Al^{3+} 24	4·25
As^{3+} 80	4·25
Sb^{3+} 24	4·25
48	4·23
Ni^{2+} 70	4·25
Zn^{2+} 65	4·25
Bi^{3+} 40	4·25
Cr^{3+} 20	4·25[b]
30	4·24[b]
10	4·22[c]
Cd^{2+} 44	4·26[d]
Co^{2+} 18	4·26[d]
Hg^{2+} 25·6	4·25[e]
50·9	4·26[e]
Mn^{2+} 5	4·26
10	4·27
Sn^{4+}, Ni^{2+}* Fe^{3+}, Zn^{2+} and Pb^{2+}	4·24

[a] Zinc as the back-titrant, masking catalysed with 1,10-phenanthroline.

[b] With about 0·5 ml of the EDTA added in excess before the first back-titration, the masking mixtures comprising 10 ml of TU, 20 ml of AA and 5 ml of TSC (or 4 drops of phen or dipy).

[c] With about 2 ml of the EDTA added in excess under the conditions for *b*.

[d] End-point is from orange to brown-red, but is very sharp.

[e] After preliminary selective determination of Hg^{2+} with only thiourea as the masking agent.

* Copper alloy (TISCO) containing 86·5% copper, 8·77% tin, 0·40% iron, 1·50% zinc, 1·16% nickel and 1·48% lead.

TABLE III.—INTERFERENCE OF IRON(III) IN THE DETERMINATION OF COPPER (12·83 mg). (EXPECTED VOLUME OF 0·05*M* EDTA LIBERATED = 4·04 ml).

Iron added, *mg*	Masking mixture				0·05*M* EDTA liberated, *ml*	End-point*
	10% TU, *ml*	1% TSC, *ml*	0·1% phen, drops	5% AA, *ml*		
3	10	—	5	4	4·04	S
5	10	—	5	4	—	N.S.
	15	—	4	2	4·04	S
10	20	—	4	2	4·04[a]	S
5	15	5	—	5	4·04	S
10	20	5	—	2	4·04[a]	S
	15	3	—	2	4·05	N.S.
	15	5	—	5	—	N.S.
15	15	6	—	—	4·04[b]	S
20	20	8	—	—	4·03[b]	S
20†	10	5	—	4	4·03	S
30†	10	5	—	5	4·01	S
	10	—	5	4	4·01	S

* S = sharp; N.S. = not sharp.

† Masking with KF before the addition of the masking mixtures.

[a] First appearance of red colour should be taken as the end-point.

[b] Titration slightly slow near the end-point.

can the interference of mercury(II) be avoided but it is also possible to carry out the consecutive determination of mercury and copper in the presence of other cations by successive masking with thiourea[10] and the present masking mixtures.

Typical results for the determination of copper in the presence of the cations mentioned, by using a masking mixture of thiourea, thiosemicarbazide and ascorbic acid with Pb^{2+} as the back-titrant, are recorded in Table II. As identical results were obtained with masking catalysed by 1,10-phenanthroline no separate table is considered necessary for those results. The determination is, however, not selective with the masking mixture containing sodium thiosulphate, where Cd^{2+} and Pb^{2+} give a drawn-out end-point and Ag^{+} causes serious interference owing to its reduction.

Small amounts of Fe^{3+} (up to 10 mg) can be tolerated by using the minimum amounts of ascorbic acid in the masking mixtures. Larger quantities of ascorbic acid impair the quality of the end-point. The ternary masking mixture with thiosemicarbazide as a constituent gives a better performance than the one with 1,10-phenanthroline (or 2,2′-dipyridyl). With preliminary masking of Fe^{3+} with potassium fluoride, either of these masking mixtures can be used. The binary masking mixture of thiourea and thiosemicarbazide is especially suitable for tolerating moderate amounts (up to 20 mg) of Fe^{3+} without any preliminary masking, with accurate results, but the titration is a bit slow near the end-point (Table III).

Acknowledgement—Professor Nazar Singh, Head of Chemistry Department, is thanked for providing research facilities.

Zusammenfassung—Eine neue Maskierungsmethode zur hochselektiven komplexometrischen Bestimmung von Kupfer(II) wurde untersucht. Sie beruht auf der Zersetzung des Kupfer-EDTA-Komplexes bei pH 5–6. Unter den verschiedenen ausprobierten Kombinationen von Maskierungsmitteln bewährten sich ternäre Maskierungsgemische mit einem Haupt-Komplexbildner (Thioharnstoff), einem Reduktionsmittel (Ascorbinsäure) und einem Hilfs-Komplexbildner (Thiosemicarbazid oder eine kleine Menge 1,10-Phenanthrolin oder 2, 2′-Dipyridyl) am besten. Ein Überschuß von EDTA wird zugegeben und die überschüssige EDTA mit Blei- (oder Zink-) nitrat und Xylenolorange als Indikator (pH 5–6) zurücktitriert. Dann wird Maskierungsgemisch zugegeben, um den Kupfer-EDTA-Komplex zu zerlegen; die freigesetzte EDTA wird wiederum mit Blei- (oder Zink-) nitrat zurücktitriert. Folgende Kationen stören nicht: Ag^+, Hg^{2+}, Pb^{2+}, Ni^{2+}, Bi^{3+}, As^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+}, Cd^{2+}, Co^{2+}, Cr^{3+} sowie nicht zu große Mengen von Fe^{3+} und Mn^{2+}. Beachtlich ist, daß Hg^{2+} und Cu^{2+} in Gegenwart anderer Kationen bequem nacheinander bestimmt werden können.

Résumé—On a effectué une étude d'une nouvelle technique de dissimulation pour le dosage complexométrique hautement sélectif du cuivre(II), basée sur la décomposition du complexe cuivre-EDTA à pH 5–6. Parmi les diverses combinaisons d'agents dissimulants essayés, les mélanges de dissimulation ternaires comprenant un agent complexant principal (thiourée), un agent réducteur (acide ascorbique) et un agent complexant auxiliaire (thiosemicarbazide ou une petite quantité de 1,10-phénanthroline ou de 2,2′-dipyridyle) ont été trouvés être les plus convenables. On ajoute un excès d'EDTA et le surplus d'EDTA est dosé en retour par le nitrate de plomb (ou de zinc) avec l'Orangé Xylénol comme indicateur (pH 5–6). Un mélange dissimulant est alors ajouté pour décomposer le complexe cuivre-EDTA et l'EDTA libéré est de nouveau dosé en retour avec le nitrate de plomb (ou de zinc). Les cations suivants n'interfèrent pas: Ag^+, Hg^{2+}, Pb^{2+}, Ni^{2+}, Bi^{3+}, As^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+}, Cd^{2+}, Co^{2+}, Cr^{3+}, ainsi que des quantités modérées de Fe^{3+} et Mn^{2+}. Le caractère remarquable est que le dosage consécutif de Hg^{2+} et Cu^{2+} peut être commodément mené en la présence d'autres cations.

REFERENCES

1. R. Přibil and F. Vydra, *Collection Czech. Chem. Commun.*, 1959, **24**, 3103.
2. R. Přibil and V. Veselý, *Talanta*, 1961, **8**, 880.
3. W. Berndt and J. Šára, *ibid.*, 1961, **8**, 653.
4. O. Budevsky and L. Simova, *ibid.*, 1962, **9**, 769.
5. R. Belcher, D. Gibbons and T. S. West, *Anal. Chim. Acta*, 1955, **12**, 107.
6. A. Ringbom, *Complexation in Analytical Chemistry*, Interscience, New York, 1963.
7. D. D. Perrin, *Organic Complexing Reagents*, pp. 81–82, Interscience, New York, 1964.
8. *Idem, op. cit.*, p. 66.
9. J. Körbl and R. Přibil, *Chem. Listy*, 1957, **51**, 667; *Collection Czech. Chem. Commun.*, 1957, **22**, 1771.
10. R. P. Singh, *Talanta*, 1969, **16**, 1447.

Talanta, 1972, Vol. 19, pp. 1429 to 1435. Pergamon Press. Printed in Northern Ireland

VOLUMETRIC DETERMINATION OF PRIMARY ARYLAMINES AND NITRITES, USING AN INTERNAL INDICATOR SYSTEM

EUGEN SZEKELY, AMALIA BANDEL and MIRIAM FLITMAN
Department of Analytical Chemistry, Negev Institute for Arid Zone Research,
Beer Sheva, Israel

(*Received* 11 *November* 1971. *Revised* 1 *May* 1972. *Accepted* 19 *May* 1972)

Summary—A new nitrite titration method is presented. The titration is performed in the presence of a standard solution of 4,4′-sulphonyldianiline and diphenylamine, which is used as an internal indicator. An intense red colour develops during the titration as a result of a simultaneous diazotization and coupling process. A very sharp end-point is given by a colour change to yellow. The titration is performed at a temperature of about 45° in the presence of large amounts of nitrate. The method is specific and precise. It is suitable for the direct volumetric determination of various easily diazotized primary arylamines, sulphonamides and other amino-compounds which can be determined by nitrite titration. It is suitable also for the indirect determination of nitrites. The method is applicable on the semimicro and macro scales.

MOST OF THE early work on arylamine determination was done in the dyestuff industry. Diazotization by direct nitrite titration is also the method of assay for most of the pharmaceutical drugs which have a free primary arylamine group and for those drugs which yield a free amino-group by hydrolysis or reduction.

In the standard methods the end-point is detected either visually with starch-iodide as an external indicator[1] or electrochemically (the dead-stop technique).[2] Different external indicators are recommended by various investigators. Some of these are tolusafranine,[3] rivanol,[4] leuco Methylene Blue,[5] and a mixture of brucine, benzidine and phosphoric acid.[6]

Attempts have been made to find suitable internal indicators for the visual detection of the end-point. Acriflavine was used by Frost,[7] diphenylbenzidine disulphonic acid by Ågren,[8] Orange IV by Vasiliev,[9] ferrocyphen by Schilt,[10] and by Banick and Valentine.[11] The potentiometric titration method was proposed by Singh andAhmed.[12] La Rocha and Waters,[13] McNaughton *et al.*[14] have reported that the method seems to give better results than those obtained when using indicators, but it is time-consuming.

Sholten and Stone[15] used an amperometric method and their results indicate that the method has some advantage over both visual and potentiometric methods. They state, however, that the end-point is somewhat sluggish and cannot be easily detected. This method (dead-stop end-point) has been introduced recently into standard methods.

The object of this investigation was to find a simple, specific, rapid and precise method, which eliminates the disadvantages and difficulties of other methods. The experiments were started with "dapsone" (4,4′-sulphonyldianiline) and diphenylamine, reagents proposed for the colorimetric determination of nitrites.[16] It was observed that a yellow colour develops when a small amount of sodium nitrite is added to an acidified solution of dapsone and that on further nitrite addition the colour fades almost completely. It was observed also that the diazotization and coupling is a simultaneous process, when a very acid solution of dapsone and diphenylamine is used at various temperatures. The resulting reddish-violet azo dye has an intense tinctorial power and is not photosensitive.[16]

EXPERIMENTAL

Solutions containing dapsone and diphenylamine were titrated in the presence of various amounts of nitric acid and the stability of nitrous acid was investigated, on the basis of the experiments of Jones and Lee.[17] The standard sodium nitrite solution was added slowly to the samples with continuous stirring. The variables were the amount of nitric acid and the temperature. When a large amount of nitric acid was present, no loss of nitrous acid was found even when the temperature of the sample solution was increased to 50°.

The addition of nitric acid alters the pH conditions. It was replaced with sodium nitrate which is preferable as it is available free from nitrite. The amount of hydrochloric acid and sodium nitrate necessary for optimal reaction conditions was established experimentally. About 45° was found to be the optimal temperature for colour development, speed of reaction and end-point detection; there is no risk of losing nitrous acid. The amount of dapsone and diphenylamine required to create an indicator solution which develops the best colour effect during the titration and at the end-point was also experimentally established.

Reagents

Standard dapsone solution 0·05*M*. Dissolve 12·5 g of reagent grade desiccated 4,4′-sulphonyldianiline in approximately 2*M* hydrochloric acid and make up to 1000 ml. The solution is stable indefinitely.

Diphenylamine solution. Dissolve 0·05 g of reagent grade diphenylamine in 100 ml of alcohol (95%).

Standard sodium nitrite solution 0·1*M*. Dissolve 7·1 g of reagent grade sodium nitrite in demineralized water, add a few drops of 0·1*M* sodium hydroxide, make up to 1000 ml, and standardize by dead-stop titration against sulphanilic acid.

Hydrochloric acid 6*M*. Mix equal volumes of reagent grade hydrochloric acid and demineralized water.

Dapsone–diphenylamine (indicator) solution. Mix 10 ml of diphenylamine solution with 100 ml of standard dapsone solution. The solution is stable for several weeks if kept in darkness.

Procedures

Amine determination. Take a sample weighed to ±0.1 mg which contains 0·2–2 meq of amine, and dissolve it in 20 ml of 6*M* hydrochloric acid in a 250-ml titration vessel. Alternatively, take an aliquot of sample solution containing 0·2–2 meq of amine, and make it about 6*M* in hydrochloric acid. Add 20 ml of sodium nitrate solution and dilute to about 100 ml. Add from a pipette 5 ml of dapsone–diphenylamine solution, heat the sample to 45° (±2°) and titrate it with 0·1*M* sodium nitrite. Use a burette with lengthened tip dipped well under the surface of the solution, and stir continuously with a magnetic stirrer. Continue the titration slowly, as the initially developed raspberry red colour turns violet. Just before the end-point, as the colour begins to fade, add the nitrite solution in 0·05-ml increments or less, at intervals of 10–20 sec. The end-point is detected by a colour change from orange-yellow to greenish-yellow. Make a blank titration using the same volumes of reagents, water and exactly the same volume of dapsone–diphenylamine solution. Subtract the volume of the standard nitrite solution used in the blank from the volume of the nitrite solution used in the titration of the sample. Calculate the content.

The method can also be applied on the semimicro scale. In this case the volume of the sample solution and of the reagents should be reduced to half of that described in the procedure. Only 2 ml of dapsone-diphenylamine solution are added and a microburette or micrometer syringe should be used.

Nitrite determination. Weigh an amount of sample containing 25-500 mg of sodium nitrite, and make up with water to 100 ml. Take a volume of 0–20 ml* of 0·05*M* dapsone solution in a 250-ml titration vessel, add 20 ml of 6*M* hydrochloric acid, 20 ml of sodium nitrate solution and 5 ml of dapsone-diphenylamine solution. Dilute to about 80 ml. Slowly add 25 ml of the sample solution from a pipette to the prepared solution, while stirring. Heat the reaction mixture to 45° (±2°). The red colour developed indicates the presence of an excess of the dapsone reagent. If the colour obtained is yellow, it is a sign of miscalculation (insufficient dapsone) and the determination should be repeated with a more dilute sample solution. Titrate the excess of dapsone with 0·1*M* sodium

---

* It is not necessary to add dapsone solution to determine less than 25 mg of sodum nitrite, since the amount of dapsone already present in the 5 ml of dapsone–diphenylamine solution is sufficient for the determination of these amounts.

nitrite as described for the amine determination. Make a blank titration with the same amount of dapsone and dapsone–diphenylamine solution, using 25 ml of water instead of the sample solution. The determination can be performed also on the semimicro scale.

Calculate the sodium nitrite content from the equation

$$\frac{(v_1 - v_2) \times f \times 4 \times 0{\cdot}069 \times 10}{W} = \frac{(v_1 - v_2) \times f \times 2{\cdot}76}{W} = A$$

where v_1 is the volume of the nitrite solution used in the blank titration (ml)
v_2 is the volume of the nitrite solution used in the sample titration (ml)
f is the factor of the standard nitrite solution
0·069 is the weight of 1 m mole of sodium nitrite (g)
W is the weight of the sample (g)
A is the amount of sodium nitrite found (%).

RESULTS

The reliability and accuracy of the method were verified on the macro and semimicro scales by titration of sulphanilic acid (purity ~ 99·9%).

A purity of 99·8–100·0% was found in 5 determinations when 1·2–1·8 meq were taken (macro method), the maximum error being 0·1%. For the semimicro method 0·04–0·05 meq was taken. The maximum error was 0·4% and the relative standard deviation 0·15% (5 determinations).

Tables I and II list the amine compounds which were determined by the procedure given.

TABLE I.—DYESTUFF INTERMEDIATES. (VALUES OBTAINED FROM AT LEAST 4 DETERMINATIONS).

	Rel. std. devn., %	Max. error, %
4-Aminoacetanilide	0·15	+0·6
8-Amino-1,3,6-naphthalene trisulphonic acid	1·2	+2
Di-(4-aminophenyl) ether	0·15	+0·5
m-Nitroaniline	0·08	+0·3
o-Nitroaniline	0·07	+0·25
p-Nitroaniline	0·08	+0·2
5-Nitro-*o*-toluidine	0·2	+0·4

TABLE II.—REAGENTS AND DRUGS. (VALUES OBTAINED FROM AT LEAST 4 DETERMINATIONS).

	Rel. std. devn. %	Max. error, %
N-Acetylsulphanilamide	0·10	+0·15
N-Amidinosulphanilamide (Sulphaguanidine)	0·05	+0·15
p-Aminobenzenesulphonamide (Sulphanilamide)	0·06	+0·2
o-Aminobenzoic acid	0·08	+0.2
p-Aminobenzoic acid	0·10	+0·25
p-Aminobenzoyldiethylaminoethanol	0·18	+0·5
hydrochloride (Procaine hydrochloride)	(semi micro determination)	
p-Aminosalicylic acid	0 10	+0.2
5-Amino-3-sulphosalicylic acid	0·08	+0·2
N-(3,4-Dimethyl-5-isoxazolyl) sulphanilamide (Sulphisoxazole)	0·15	+0.35
Ethyl aminobenzoate	0·08	+0·2
N-(6-Methoxy-3-pyridazinyl)sulphanilamide (Sulphamethoxypridazine)	0·18	+0.3
N-(4-Methyl-2-pyrimidyl)sulphanilamide (Sulphamerazine)	0·15	+0·3
N-2-Pyridylsulphanilamide (Sulphapyridine)	0·12	+0·2
2-Sulphanilamidopyrimidine (Sulphadiazine)	0·10	+0·15
N-2-Thiazolylsulphanilamide (Sulphathiazole)	0·12	+0·2

A very sharp end-point was detected in all these determinations, except in the titration of 8-amino-1,3,6-naphthalene trisulphonic acid, where the colour turns to orange-yellow at the end of the titration. In this case the error is about ±1%.

DISCUSSION

In Scheme 1 is shown the course of the reactions when dapsone–diphenylamine solution is titrated under the conditions given in the procedures.

Reactions

Phase 1. Dapsone is diazotized. The reaction process is accelerated by heating. The product is a yellow tetra-azonium salt.

Phase 2. Most of the tetra-azonium salt is hydrolysed in the course of the titration and 4,4′-dihydroxydiphenylsulphone forms (probably), which is colourless. A very small part of the yellow tetra-azonium salt is coupled at the same time with diphenylamine. The coupling process is faster than the hydrolysis and the intense raspberry red bis-diphenylamino-4,4′-azodiphenylsulphone forms.[16]

Phase 3. The dye product splits slowly into diphenyalmine and 4,4′-dihydroxydiphenylsulphone. The effect is that the colour fades towards the end of the titrations.

Phases 4–5. The liberated diphenylamine is oxidized by the nitrous acid to diphenylbenzidine (colourless) then to diphenylbenzidine violet near the end of the titration, consequently the colour of the sample solution turns to bluish-violet.

Phase 6. The diphenylbenzidine violet is nitrosated to the yellow dinitrosidiphenylbenzidine.[18] (End-point.)

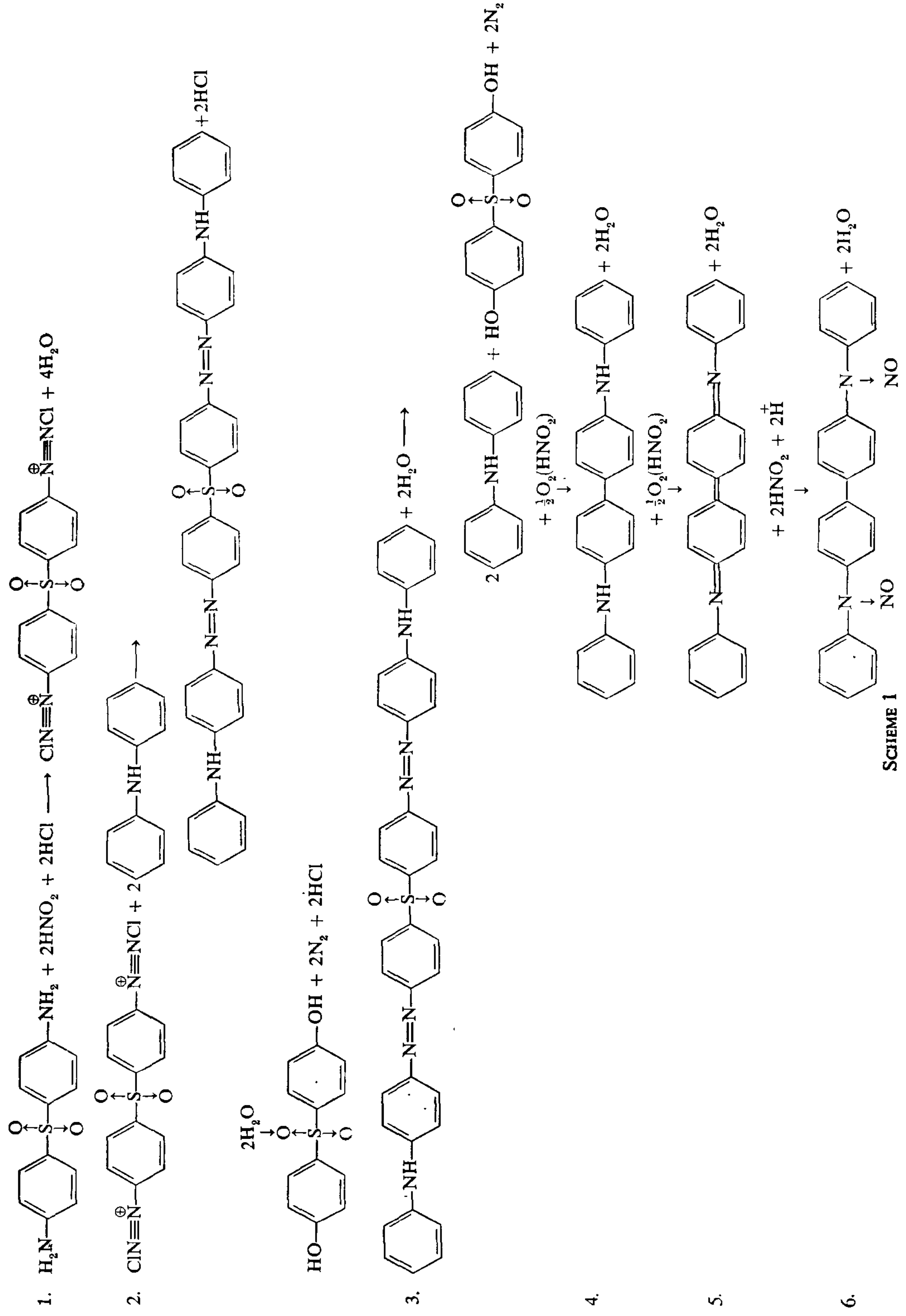
These reactions take place also when a primary arylamine is titrated in the presence of the dapsone–diphenylamine solution. If the amine is easily diazotized, phase 1 is a simultaneous diazotization of both the amine product and of the dapsone. Phases 2–6 take place in similar stages and have the same velocity. The end point is also similar.

The amount of $0{\cdot}1M$ sodium nitrite required to produce a colour change from bluish-violet to yellow is 0·03 ml, if 5 ml of dapsone–diphenylamine solution are taken, and only 0·012 ml when 2 ml are taken (semimicro determination). It was found experimentally also that these calculated amounts of nitrite are necessary to produce the ultimate colour changes.

Effect of nitrate and of temperature. It was found that it is necessary to add nitrate in order to prevent loss of nitrous acid. It was observed that the presence of nitrate has a second and very important effect.

Dapsone–diphenylamine solutions, and also amine samples in the presence of dapsone–diphenylamine solution, were titrated in the absence of sodium nitrate. It was found that not only a loss of nitrite occurs, but the ultimate phases (see Scheme I) do not take place. The violet colour of the sample does not disappear and consequently a precise end-point cannot be detected. This phenomenon can be explained by the fact that under the conditions of the procedure the diphenylamine is easily oxidizable only in the presence of large amounts of nitrate ion. The diphenylbenzidine violet is not nitrosated to the yellow nitroso product in the absence of nitrate ion.

Experiments were made with diphenylamine solutions acidified with hydrochloric acid. When no nitrate ion was present in the solution, no colour developed after the addition of nitrite either at room temperature or at about 45°. In the presence of a sufficient amount of sodium nitrate a violet colour develops slowly, which intensifies in


1.
+ 2HNO₂ + 2HCl
+ 4H₂O
2.
+ 2
+2HCl
2H₂O
+ 2N₂ + 2HCl
3.
+ 2H₂O
+ 2N₂
4.
+ ½O₂(HNO₂)
+ 2H₂O
5.
+ ½O₂(HNO₂)
+ 2H₂O
6.
+ 2HNO₂ + 2H⁺
+ 2H₂O
NO
NO

SCHEME 1

a few minutes and turns grey, greenish-grey and than greenish-yellow (at room temperature). The colour development is faster at higher temperatures; in this case the violet colour appears instantaneously and begins to fade in a few seconds and turns greenish-grey and then to greenish-yellow in less than one minute. The same colour developments also take place when an amine is determined by the procedure described.

Effect of dapsone. Experiments were made to determine sulphanilic acid under the conditions described in the procedure, but omitting dapsone. No colour development occurs in phase 1. A pink colour develops in the course of the titration and the colour turns to bluish-violet and then to grey near the end of the titration, but it is not possible to detect a precise end-point.

APPLICATION OF METHODS, CONCLUSIONS

The determination of colourless or slightly coloured amino compounds is uncomplicated and rapid by this method. The sensitivity is high, so it is possible to determine with accuracy also small amounts of samples. The method is less suitable for the determination of naphthylamines, where an intense colour may be developed during the diazotization process. The method is not applicable for samples which are coloured owing to the presence of impurities or of decomposition products. Nitrites are easily determined by the procedure described. The determinations are not affected by the presence of reductants such as sulphurous acid, formic acid, hydroquinone, nor by alcohol or acetone.

Oxidizing agents must be absent. Bromide does not interfere even if present in large amounts, but the use of potassium bromide as catalyst is not necessary, since the velocity of the reactions is quite satisfactory.

Zusammenfassung—Es wird eine neue Nitrit-Titrierungsmethode gebracht. Die Titrierung wird mit einer normalen Lösung von 4,4′-Sulfonyl-Dianilin und Diphenylamin durchgeführt, welche als innerer Indikator benutzt wird. Während der Titrierung entwickelts sich eine kräftige rote Färbung infolge der gleichzeitigen Diazotierung und des Verbindungsprozesses. Durch Farbwechsel auf gelb ergiebt sich ein sehr scharf ausgesprochener Endpunkt. Die Titrierung erfolgt bei einer Temperatur von etwa 45° in Gegenwart von grossen Nitratmengen. Das Verfahren ist definitiv und genau. Es ist zur direkten Bestimmung von Volumen von verschiedenen, leicht diazotierten, primären Acrylaminen, Sulfoamiden und anderen Aminoverbindungen geeignet, welche durch Nitrittitrierung bestimmt werden können. Es ist auch zur indirekten Bestimmung von Nitriten geeignet. Das Verfahren kann in semi-mikro und Grösstniederschlägen verwandt werden.

Résumé—On présente une nouvelle méthode de dosage au nitrite. Le titrage est mené en la présence d'une solution titrée de 4,4′-sulfonyldianiline et diphénylamine, qui est utilisée comme indicateur interne. Une coloration rouge intense se développe durant le titrage comme résultat d'un processus simultané de diazotation et copulation. Un point de fin de dosage très net est fourni par un virage de coloration au jaune. Le titrage est réalisé à une température d'environ 45° en la présence de grandes quantités de nitrate. La méthode est spécifique et précise. Elle convient au dosage volumétrique direct de diverses arylamines primaires aisément diazotées, de sulfamides et d'autres composés aminés qui peuvent être déterminés par titrage au nitrite. Elle convient aussi au dosage indirect des nitrites. La méthode est applicable aux échelles semimicro et macro.

REFERENCES

1. *United States Pharmacopeia XVII*, 1965, pp. 882–83.
2. *British Pharmacopoeia*, 1968 Ed. pp. 1234-35.
3. P. Carboni, *Chim. e Ind.*, 1954, **36**, 825.
4. M. Svach and J. Zýka, *Chemiker-Ztg.*, 1955, **79**, 781.
5. E. A. Soulez, *An. Assoc. Quim. Arg.*, 1942, 96.
6. K. Grissmann, *Mikrochim. Acta*, 1963, 782.
7. H. F. Frost, *Analyst*, 1943, **68**, 51.
8. A. Ågren, *Svensk Farm Tids.* 1951, **55**, 229; *Chem. Abstr.*, 1951, **45**, 6127*c*.
9. R. Vasiliev, A. Cosmin, I. Burnea and M. Manyu, *Farmacia*, 1961, **9**, 43.
10. A. A. Schilt, *Anal. Chem*, 1964, **36**, 1805.
11. W. M. Banick and J. R. Valentine, *J. Pharm. Sci.*, 1964, **53**, 1242.
12. B. Singh and G. Ahmed, *J. Indian Chem. Soc.*, 1938, **15**, 416.
13. J. P. La Rocha and K. L. Waters, *Am. Pharm. Assoc. Sci.* Ed., 1950, **39**, 521.
14. G. A. McNaughton, M. J. Huston and B. E. Riedel, *Can. Pharm. J.*, 1951, **84**, 744.
15. H. G. Scholten and K. W. Stone, *Anal. Chem.*, 1952, **24**, 749.
16. E. Szekely, *Talanta*, 1968, **15**, 795.
17. D. O. Jones and H. P. Lee, *Ind. Eng. Chem.*, 1924, **16**, 948.
18. F. Kehrmann and St. Micewicz, *Ber.*, 1912, **45**, 2650.

Talanta, 1972, Vol. 19, pp. 1437 to 1441. Pergamon Press. Printed in Northern Ireland

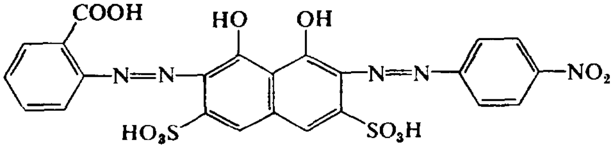
SHORT COMMUNICATIONS

Arsenazo III and its analogues—VII. Colour reactions of the rare earth elements with a new reagent—Carboxynitrazo

(*Received* 28 *November* 1969. *Revised* 26 *July* 1970. *Accepted* 21 *October* 1971)

SPECTROPHOTOMETRIC methods are widely used for the determination of the rare earth elements,[1] mono- and 2,7-bisazo-derivatives of chromotropic acid being extensively employed.[2-4] Almost all well-known reagents react with all the rare earths, but small differences, observed in some cases,[5] may enable one element to be determined in the presence of the others.

In this paper the new reagent carboxynitrazo—the 2,7-bisazo-derivative of chromotropic acid—is suggested for the determination of the rare earth elements.



This reagent has been recommended for the determination of strontium, barium and sulphate.[6,7] With it some rare earth elements give coloured reaction products with very different analytical characteristics. The difference is greatest for the elements of the cerium and yttrium subgroups.

EXPERIMENTAL

Reagents

Carboxynitrazo—2,7-bisazo-chromotropic acid. The synthesis, purification, checking of purity and properties of Carboxynitrazo have been reported earlier,[6,7] as have the acid dissociation constants.[8-10] In the present work $0{\cdot}5 \times 10^{-3}M$ and $0{\cdot}25 \times 10^{-3}M$ solutions of reagent were prepared and passed through a cation-exchange column, KY-2, in the H-form, to remove possible impurities such as calcium and other elements.

Rare earths. The solutions of the rare earth elements were prepared by dissolution of exactly weighed amounts of the metals (La, Pr, Nd and Y), or oxides (Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) in hydrochloric acid. The concentrations were checked spectrophotometrically and complexometrically.

RESULTS

Spectrophotometric investigation of the complexes of carboxynitrazo with the rare earth elements

The relevant absorption spectra, conditions for reactions and optical constants are given in Figs. 1–4 and Table I.

TABLE I.—SOME CHARACTERISTICS OF COLOUR REACTIONS OF CARBOXYNITRAZO WITH RARE-EARTH ELEMENTS

$\lambda_{\max,R} = 560$ nm, $\lambda_{\max,MeR} = 730$ nm, $\Delta\lambda = 170$ nm

Element	Optimum pH	Molar absorptivity, *l.mole*$^{-1}$*.cm*$^{-1}$	Composition Me:R
La	2–3·5	$1{\cdot}56 \times 10^5$	1:2
Ce	1·8–3·1	$1{\cdot}60 \times 10^5$	—
Pr	2·2–3·5	$1{\cdot}55 \times 10^5$	1:2
Nd	2·2–3·5	$1{\cdot}63 \times 10^5$	—
Sm	2·7–4·2	$1{\cdot}27 \times 10^5$	1:2
Eu	3–4·5	$1{\cdot}22 \times 10^5$	1:2·4
Gd	3·5–4·8	$1{\cdot}16 \times 10^5$	—
Tb	4·0–4·4	—	—
Dy			
Ho			
Er	no reaction		
Yb			
Y			

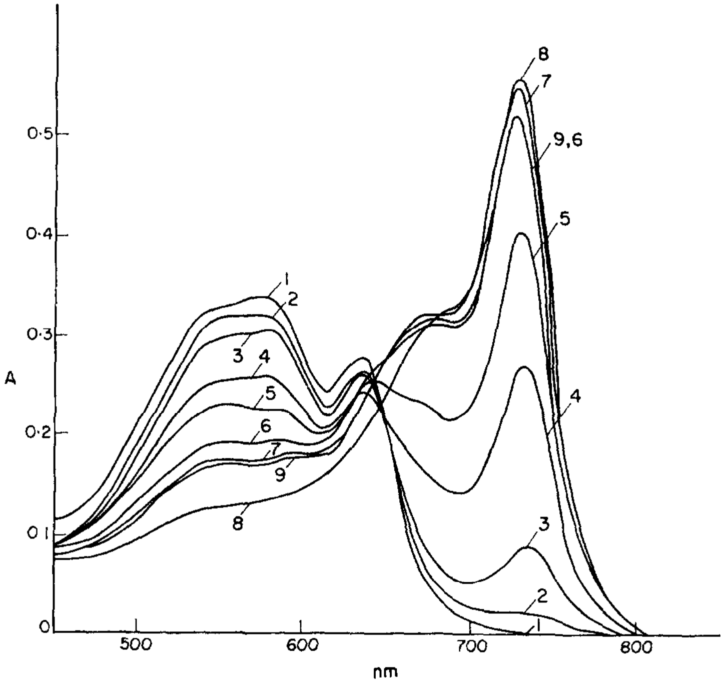


FIG. 1.—Absorption spectra of Carboxynitrazo and its complexes. Reagent (1) and in the presence of Y, Yb (1), Er, Ho, Dy (2), Tb (3), Gd (4), Eu (5), Sm (6), Nd, Pr (7), La (8), Ce (9) at pH 3·0 Concentration: $[R] = 1 \times 10^{-5}M$; $[Me] = 0{\cdot}5 \times 10^{-5}M$; 10—mm cell; recorded against water.

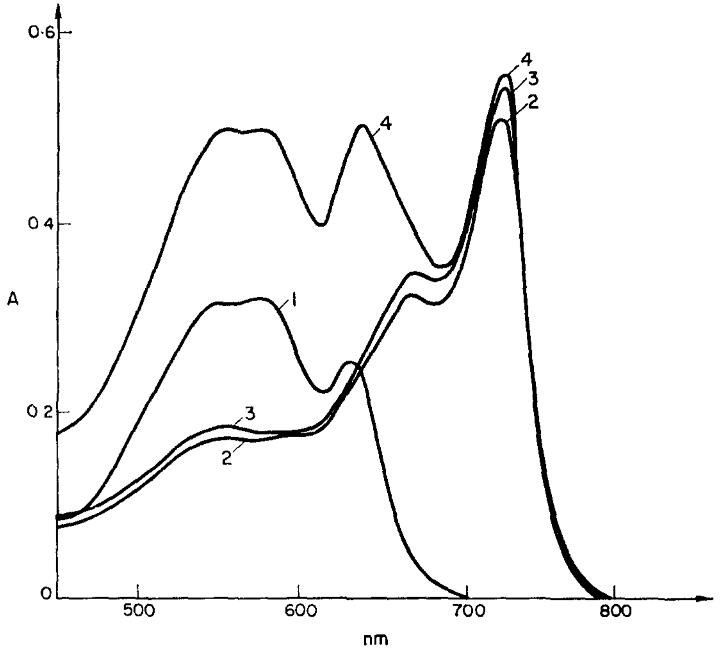


FIG. 2.—Absorption spectrum of Carboxynitrazo (1) and its complexes with La at various Me:R ratios:
2—Me:R = 1:2; *3* and *4*—Me:R = 1:4.
1, *2* and *4* recorded against water,
3 recorded against two parts of reagent.
$[M] = 0{\cdot}5 \times 10^{-5}M$; pH 3·0.

The influence of temperature, time and addition of some organic solvents

The absorbance of the complexes usually varies with time, especially for 20 min after preparation of the solutions. With Ce, La, Pr and Nd the absorbance reaches a constant value in ~30 min, with the other elements which form colours the reaction takes 1–2 hr. For the solutions containing Y, Yb, Er, Ho and Dy colour development is not observed even after 24 hr. Heating of the solution and addition of organic solvent (acetone, ethanol, propanol) results in a decrease of the absorbance of the solutions at 730 nm.

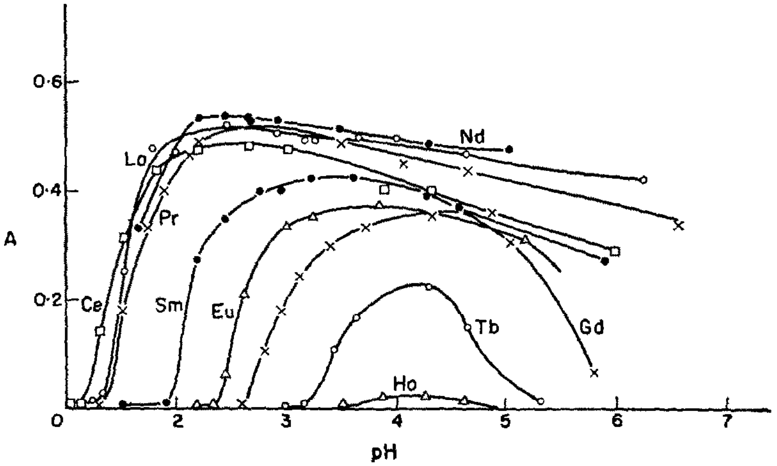


FIG. 3.—The effect of pH on the colour reaction between rare earth elements and Carboxynitrazo.
$[R] = 2 \times 10^{-5}M$, $[Me] = 0{\cdot}4 \times 10^{-5}M$, $\lambda = 730$ nm.

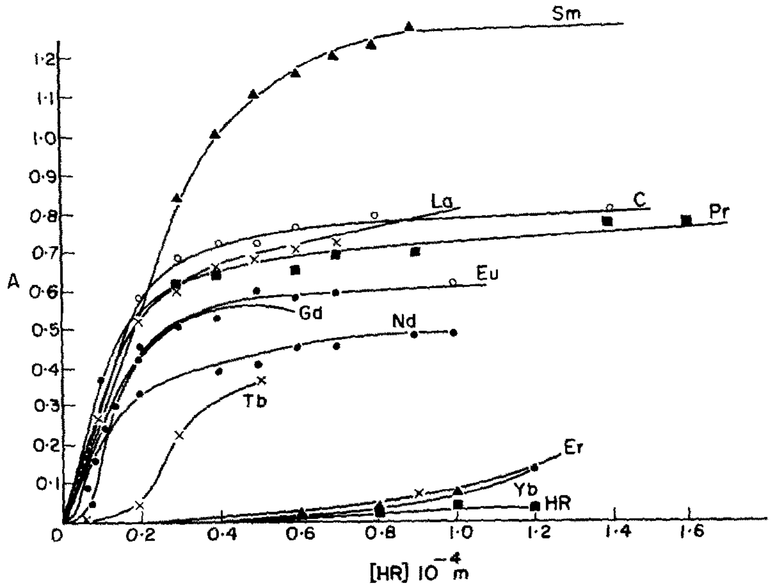


FIG. 4.—The effect of the concentration of Carboxynitrazo on the colour reaction with the rare earth elements.
$[Me] = 0{\cdot}5 \times 10^{-5}M$ ($[Sm] = 1 \times 10^{-5}M$), pH 2·8–3·0; $\lambda = 730$ nm.

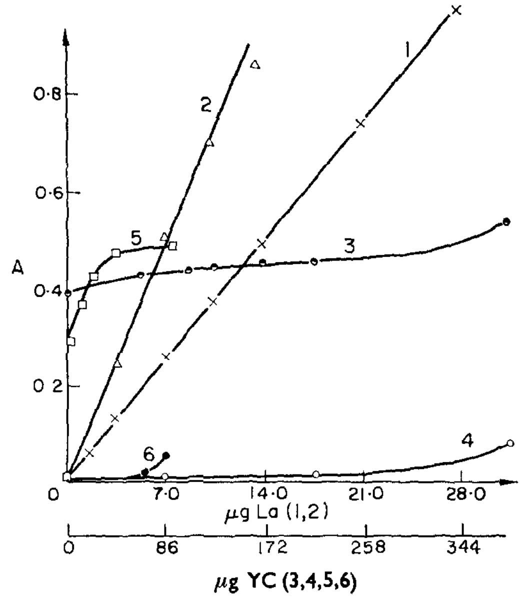


FIG. 5.—Colour reactions of Carboxynitrazo with La at various concentrations of Yb. $[R] = 3 \times 10^{-5}M$.

1—La variable, pH 2·0 and 3·0
2—La variable, 173 μg of Yb, pH 3·0
3—Yb variable, 10 μg of La, pH 2·0
4—Yb variable, pH 2·0
5—Yb variable, 7·7 μg of La, pH 3·0
6—Yb variable, pH 3·0.

Mutual influence of elements of the Y- and Ce-groups

The curves for A *vs.* pH (Fig. 3) and A *vs.* [R] (at constant [Me]) (Fig. 4) show a possibility of the determination of the Ce-group elements in presence of the Y-group elements. We checked such a possibility by using a lanthanum–ytterbium mixture as an example. Measurements were made at pH 2·0 and 3·0, which is the range for the maximum colour reaction for lanthanum, whereas the absorbance of the ytterbium solutions is equal to that of the reagent itself.

However, at 730 nm the absorbance of the solutions containing both ytterbium and lanthanum is greater than that of the analogous solutions of ytterbium-free lanthanum. This effect is more pronounced at pH 3·0 than at pH 2·0. For example, at the ratio Yb:La $\sim$ 2:1 the increase in absorbance amounts to almost 50% at pH 3.0 but only 7–10% at pH 2·0. The absorbance at 730 nm increases with increasing ytterbium concentration only up the ratio Yb:La $\sim$ 2:1 (Fig. 5). The calibration curves at pH 3·0 in the presence and absence of ytterbium (Fig. 5, curves 1, 2) have different slopes. At pH 2·0 these curves almost coincide with each other and permit the determination of lanthanum in the presence of ytterbium. So a 25-fold excess of ytterbium does not interfere with the determination of 10 μg of lanthanum if water or reagent solution are used as reference solutions, and a 40-fold excess can also be dealt with if the reagent and Yb is used as a blank. The permissible concentration of the ytterbium can be increased provided that the pH is decreased, although in this case the sensitivity of the lanthanum determination is slightly decreased.

Probable mechanism of reactions

It has been noted that the colour reactions of alkaline earths and some other elements with 2,7-bisazo derivatives of chromotropic acid are of three basic types.[6,11] Each of these types can take place for the same pair of the components (metal and reagent) depending on conditions (pH, concentration of the components, with or without organic solvents, *etc*).

From consideration of the spectral characteristics, and also the influence of temperature and additions of organic solvents on the spectra, it can be noted that the reactions of rare earths with Carboxynitrazo described in this paper resemble reactions of the alkaline earths with analogous reagents, proceeding according to the third type of reaction.

On this basis the structures of the corresponding complexes are expected to be similar.

V. I. Vernadsky Institute of Geochemistry
and Analytical Chemistry
U.S.S.R. Academy of Sciences
Moscow

S. B. Savvin
T. V. Petrova
P. N. Romanov

Summary—A new reagent, Carboxynitrazo, gives a colour reaction with some rare earth elements. For the individual rare earth elements the sensitivities of the reactions are very different. The difference is greatest for the elements of the Ce- and Y-subgroups. For the first subgroup the molar absorptivities are about 16×10^4 l. mole^{-1} cm^{-1}, whereas most of the elements of the Y-group do not give any colour reaction. A possible procedure for the determination of lanthanum in the presence of ytterbium is discussed.

Zusammenfassung—Ein neues Reagens, Carboxynitrazo, gibt eine Farbreaktion mit einigen seltenen Erden. Für die einzelnen seltenen Erden ist die Empfindlichkeit der Reaktion sehr verschieden. Am größten ist der Unterschied bei den Elementen der Cer- und Yttrium-Untergruppen. Bei der ersten Untergruppe liegen die molaren Extinktionskoeffizienten um $16 \cdot 10^4$ l. mol^{-1} cm^{-1}, wogegen die meisten Elemente der Y-Gruppe gar keine Farbreaktion geben. Ein mögliches Verfahren zur Bestimmung von Lanthan in Gegenwart von Ytterbium wird diskutiert.

Résumé—Un nouveau réactif, le Carboxynitrazo, donne une réaction colorée avec quelques éléments des terres rares. Pour les éléments individuels des terres rares, les sensibilités des réactions sont très différentes. La différence est la plus grande pour les éléments des sous-groupes Ce et Y. Pour le premier sous-groupe, les coefficients d'absorption moléculaire sont d'environ 16×10^4 l.mole.cm^{-1}, tandis que la plupart des éléments du groupe Y ne donne pas de réaction colorée. On discute d'une technique possible pour le dosage du lanthane en résence d'ytterbium.

REFERENCES

1. N. S. Poluektov and L. I. Kononenko, *Spectrophotometric methods for the determination of rare earth elements*, Kiev, 1968.
2. S. B. Savvin. *Arsenazo III. Metodi fotometricheskogo opredeleniya redkikh i aktinidnykh elementov*, Atomizdat, Moscow, 1966.
3. L. Sommer and M. Hnilickova, *Folia, Chemia*, 1964, **5**, 113.
4. S. B. Savvin, R. F. Propistsova and R. V. Strelnikova, *Zh. Analit. Khim.*, 1969, **24**, 31.
5. Ni Chjao-Ai, *Dissertation*, GEOHI AN SSSR, 1963.
6. S. B. Savvin and T. V. Petrova, *Zh. Analit. Khim.*, 1969, **24**, 177.
7. T. V. Petrova, N. Khakimkhodzhaev and S. B. Savvin. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 259.
8. S. B. Savvin, T. V. Petrova and E. L. Kuzin, *ibid.*, 1969, 290.
9. T. V. Petrova, S. B. Savvin and N. Khakimkhodzhaev, *Zh. Analit. Khim.*, 1970, **25**, 226.
10. *Idem, ibid.*, 1970, **25**, 2110.
11. S. B. Savvin, E. L. Kuzin, T. V. Petrova and N. Khakimkhodzhaev, *ibid.*, 1969, **24**, 1325.

Talanta, 1972, Vol. 19, pp. 1442 to 1444. Pergamon Press. Printed in Northern Ireland

Application of photon-counting in atomic-absorption spectrophotometry

(*Received* 14 *January* 1972. *Accepted* 16 *February* 1972)

PHOTON-COUNTING is usually employed for the detection and measurement of very weak radiation levels, where the stability and integral nature of the method make it superior to other techniques.[1] It can, however, be used in the presence of quite high radiation levels, provided that the pulse rate does not exceed the linear counting range. An excellent example of this is in atomic-absorption spectrometry where pulse pile-up[2] is not a problem because the number of photons striking the detector actually decreases during the signal period. Malmstadt *et al.*[3] demonstrated the application of photon-counting to solution absorption spectrophotometry and gave statistical equations relating the signal:noise ratios to the count-rates. These equations however, as this study shows, are not valid in their simplest form for atomic-absorption spectrometry where extra noise factors such as flame flicker and variations in nebulization are present.

EXPERIMENTAL

Apparatus

The photon-counting system used for this work has been described elsewhere[4] and incorporates a cooled (−40°) high-gain photomultiplier coupled directly to a frequency meter. This has advantages over the more conventional system consisting of a photomultiplier, amplifier, discriminator and frequency meter.[2,5] Cadmium was chosen for atomic-absorption measurements, as hollow-cathode lamps for this element are usually quite stable and have high line-to-background ratios. The dispersive system used was a Hilger and Watts D330 monochromator having a grating with 1200 lines/mm blazed at 330 nm. A hydrogen/argon/air diffusion flame stabilized on a 5-cm slot burner fitted to the nebulizer of a Perkin–Elmer 290 atomic-absorption spectrometer served as a free atom reservoir. The flow-rates and pressures were: hydrogen 8·0 l./min at 3 psig, argon 4·0 l./min at 30 psig. Radiation from the hollow cathode lamp was focussed at the centre of the flame *ca.* 4 cm above the burner slot. The image was refocussed on the entrance slit of the monochromator, which was set to transmit the 228·8-nm resonance line of cadmium.

Procedures

Direct current measurements. Direct measurements were made by connecting the output of the photomultiplier (all atomic-absorption measurements were made with the photomultiplier cooled) directly to a Servoscribe recorder having a 100 kΩ load resistor across its input.

An attempt to determine the optimal slit-width showed that the signal:noise ratio increased steadily as the slit-width was increased. Drawing large currents from a photomultiplier results in energy trapping in the photo-cathode (which causes increased dark-current and noise) and therefore the slit-width was set so that the output current did not exceed 10 μA. The cadmium hollow-cathode lamp was operated at 3 mA *via* the lamp supply of a Perkin–Elmer 290B atomic-absorption spectrophotometer. The power supply had a 50-Hz modulation which was monitored by the recorder and proved to be the limiting noise component of the d.c. signal. The recorder gain was set so that the chart represented 0–100% transmission. A working curve was constructed for concentrations of 0·05–10·0 ppm Cd; the linear range was 0·05–4·0 ppm Cd and the detection limit was 0·05 ppm Cd. The concentration range studied was limited by the difficulty of making precise readings on a simple d.c. system at high absorbances (10 ppm Cd ≡ 0·76 absorbance units).

Photon-counting measurements. The error in reciprocal transmission $1/T$ is given by the equation:

$$\left(\frac{S_{1/T}}{1/T}\right)^2 = \left(\frac{S_{N_0}}{N_0}\right)^2 + \left(\frac{S_{N_t}}{N_t}\right)^2 \qquad (1)$$

where S_i is the standard deviation of the i_{th} variable, N_0 is the reference-beam count-rate and N_t is the transmitted-beam count-rate.

The equation shows that the precision of $1/T$ can be increased either by increasing the count-period or the count-rate. Based on this criterion the slit-width was set so that with the longest counter gating-time of 10 sec the register would be nearly filled. The reference-beam count-rate in most of our experiments was *ca.* 89700/sec, which corresponded to a slit-width of 0·03 mm, compared with 0·05 mm used for the d.c. measurements.

First, an analytical working curve was constructed for concentrations of 0·05–100 ppm Cd, the linear range being 0·05–30·0 ppm Cd (36·0 ppm Cd ≡ 0·76 absorbance units) and the detection limit 0·02 ppm Cd. The lower detection limit obtained by photon-counting can be attributed to the integral nature of the method, which effectively removes the noise component derived from the 50-Hz lamp modulation. Thirty 10-sec readings of the reference-beam count were taken and analysis yielded the following results; average count 896317, standard deviation 2841, and relative standard deviation 0·32%, which shows that in terms of a 10-sec period the lamp was quite stable.

"Normal" statistical populations have the property that the standard deviation of the sample mean decreases as the square root of the number of samples taken increases. In counting experiments, the number of samples taken is equivalent to the count period so that the precision of measurement is inversely proportional to the square root of the count period. The signal-noise ratio will therefore be proportional to the square root of the count-period t:

$$\frac{\text{signal}}{\text{noise}} = \frac{N_S t^{1/2}}{(N_s + 2N_0)^{1/2}} \tag{2}$$

where $N_S = N_0 - N_t$.

An experiment was carried out to investigate whether in practice the signal:noise ratio increases in proportion to $t^{1/2}$. Repetitive spraying (30 times) of solutions containing 1·0 ppm Cd, for count periods of 0·1, 1·0 and 10·0 sec yielded the following results; for the 0·1-sec count signal:noise ratio was 420·6, for the 1·0-sec count 2199 and for the 10·0-sec count 2243. The large increase in signal:noise ratio which occurred between the 0·1 and 1·0-sec count-periods can be attributed to the increasing noise contribution of the lamp modulation at short count-periods. Once the count-period had reached 50 times the modulation period (*i.e.* 1 sec) the results showed an increase in the signal: noise ratio somewhat less than that predicted by theory. This has also been our experience[4] when studying atomic-fluorescence signals, with unmodulated sources. The reason for this is the difficulty of maintaining experimental conditions constant during the longer count-periods, and during the whole sampling time which amounted to 30 min for the 10·0-sec count-periods. Drift in the source and monochromator, *etc*, is a serious limitation in obtaining precise results from integral measurements, because the error is cumulative. Random interference, *e.g.*, electrical and cosmic radiation, is also a problem, because although it may prove to obey Poisson statistics, the time-scale is so different from that of photon arrival that a particular interference may be a unique event in terms of a sampling period.

The unorthodox use of a modulated reference beam for d.c. and integral measurement was deliberate, since it clearly demonstrated the ability of photon-counting (and other integration techniques) to improve significantly measurements made on signals having poor short-term stability, particularly if the instability is periodic in nature.

RESULTS AND DISCUSSION

Error analysis for atomic absorption

Atomic-absorption measurements by photon-counting can be made in two ways; at low absorbances (less than about 0·07) the concentration is directly proportional to the number of absorbed photons, whilst at higher absorbances it is necessary to plot absorbance *vs*, concentration to obtain good linearity. In the first instance the analysis of the results is the same as that for atomic-fluorescence and emission spectrometry, the signal:noise ratio being given by equation (2).

When the noise is somewhat worse than that predicted by counting statistics, it is necessary to measure the standard deviation of N_s experimentally. For values of absorbance Malmstadt *et al.*[3] defined the error in absorbance (% EA) as:

$$\%\,\text{EA} = \frac{\log\,(1/T + S_{1/T}) - \log\,(1/T)}{\log\,(1/T)} \times 100 \tag{3}$$

where $S_{1/T}$ can be derived from equation (1) which is quite general and not specific to counting statistics. The value of EA has a shallow minimum at about 1·0 absorbance units and high precision can be obtained in this region. Table I shows the error, calculated by the various methods described, for the 1·0-ppm Cd solution, using 1·0 and 0·1-sec count-periods. It is clear that certain conclusions can be drawn from this table.

1. As expected, the error predicted by counting statistics is apt to be low, especially for systems exhibiting a large experimental error (*e.g.*, 0·1-sec count-period with 50-Hz lamp modulation).

2. The experimental values show good correlations between the various methods, but some comment can be made with regard to the method of derivation. Values for absorbance errors depend

on the ratio I_0/I_t, whereas errors in N_s depend on the difference $I_0 - I_t$. Over the experimentally useful ranges of I_0 and absorbance calculations show that I_0/I_t is less sensitive than $I_0 - I_t$ to changes in I_0 and therefore greater precision can be expected from absorbance measurements (on single-beam instruments).

TABLE I.—COMPARISON OF RELATIVE STANDARD DEVIATIONS.

	Relative standard deviation of N_s, %		Relative standard deviation of absorbance, %	
	1-sec	0·1-sec	1·0-sec	0·1-sec
Counting statistics	4·91	14·2	3·95	14·0
Experimental	4·55	23·8	4·74	19·9
From equations (1) and (3) and the experimental values S_{N_0} and S_{N_t}	—	—	6·53	18·6

In conclusion, great care must be exercised when predicting errors from photon-counting in atomic spectrometric experiments. Equations calculated on the basis of simple Poisson statistics are usually inadequate because they relate to only one noise component, which is not normally the dominant one in these experiments. Previous work in this laboratory[4] has shown that noise contributions from sources such as flame flicker, variations in the solution sampling (either by nebulizers or one-shot devices such as a platinum filament) and apparatus drift, can be several times greater than Poisson or shot noise. Under these conditions it is necessary to measure the precision experimentally, at least initially, in order to determine what the noise contributions are, and whether the simple and convenient equations of counting statistics are applicable.

Acknowledgement—We wish to thank the Science Research Council for the award of a studentship to one of us (B. L. S.) and for a research grant to purchase apparatus used in this study.

Chemistry Department
Imperial College of Science and Technology
London, S.W.7

R. M. DAGNALL
B. L. SHARP
T. S. WEST

Summary—An analysis is given of the statistics of photon-counting as a means of making measurements in atomic-absorption spectrometry. It is concluded that the simple application of Poisson counting statistics may give an over-optimistic estimate of the error, since other sources of error, such as flame flicker and variable nebulization rate, may be more significant.

Zusammenfassung—Es wird eine Analyse der Statistik über Photonzählung als ein Mittel zur Durchführung von Messungen in Atomabsorption Spektrometrie gebracht. Man kommt zu dem Schluss, dass die einfache Anwendung von Zählstatistiken nach Poisson eine überoptimistische Schätzung des Fehlers ergeben könnte, da andere Ursachen für Fehler, wie Flickern der Flamme und veränderlicher Zerstäubungsgrad bezeichnender sein können.

Résumé—On donne une analyse des statistiques de comptage de photons comme moyen de faire des mesures en spectrométrie d'absorption atomique. On en conclut que la simple application des statistiques de comptage de Poisson peut donner une estimation par trop optimiste de l'erreur, car d'autres sources d'erreur, telles que le vacillement de la flame et la vitesse de nébulisation variable peuvent être plus importantes.

REFERENCES

1. G. A. Morton, *Appl. Opt.*, 1968, **7**, 1.
2. D. Alger, R. M. Dagnall, B. L. Sharp and T. S. West, *Anal. Chim. Acta*, 1971, **57**, 1.
3. M. L. Franklin, G. Horlick and H. V. Malmstadt, *Anal. Chem.*, 1969, **41**, 2.
4. R. M. Dagnall, B. L. Sharp and T. S. West, *Nature*, 1972, **235**, 65.
5. *Idem, ibid.*, 1971, **234**, 69.

Talanta, 1972, Vol. 19, pp. 1445 to 1448. Pergamon Press. Printed in Northern Ireland

Some new applications of ferroin as redox indicator in titrations with dichromate

(*Received* 11 *February* 1972. *Accepted* 22 *February* 1972)

DESPITE the advantage of being a primary standard, potassium dichromate has found limited application as an oxidizing titrant. This has hitherto been attributed to the low oxidation potential of the system under normal conditions,[1] but recently it has been shown[2] that some reactions with dichromate may fail for kinetic rather than for thermodynamic reasons; further the reported conditional potential[3] of the Cr(VI)/Cr(III) system is shown to be useless for calculations of equilibrium constants of dichromate reactions. Ferroin is close to an ideal reversible indicator with excellent indicator properties; unfortunately its slow reaction with dichromate has prohibited its use as an indicator in dichromate titration of reducing agents other than iron(II). A critical study of the behaviour of ferroin in the iron(II)–dichromate titration[4] has revealed some interesting points. The catalytic effect of iron(III) on the indicator oxidation is utilized in a procedure for the dichromate determination of arsenic(III), and it is also possible to use ferroin as redox indicator in the dichromate titration of hydroquinone, ferrocyanide, uranium(IV) and molybdenum(V) by suitable choice of conditions.

Arsenic(III) reacts rather sluggishly with cerium(IV) or permanganate; and hence either osmium tetroxide[5] or iodine monochloride[6] is used as catalyst in titrimetric procedures based on these reactions. The reaction between arsenic(III) and chromium(VI) seems to proceed through the following intermediate steps:

$$\mathrm{Cr(VI)} + \mathrm{As(III)} \rightarrow \mathrm{Cr(IV)} + \mathrm{As(V)} \tag{1}$$

$$2\mathrm{Cr(IV)} + \mathrm{As(III)} \rightarrow 2\mathrm{Cr(III)} + \mathrm{As(V)} \tag{2}$$

Step (2) is slow and probably more complex. However this reaction is used to induce the rapid and complete oxidation of manganese(II) and cerium(III) under suitable experimental conditions;[7] these reactions are believed to proceed through reaction steps (1) and (3), the latter being faster than step (2).

$$\left.\begin{array}{l}\mathrm{Cr(IV)} + \mathrm{Mn(II)} \rightarrow \mathrm{Cr(III)} + \mathrm{Mn(III)}\\ \mathrm{Cr(IV)} + \mathrm{Ce(III)} \rightarrow \mathrm{Cr(III)} + \mathrm{Ce(IV)}\end{array}\right. \tag{3}$$

In view of the sluggishness of the reactions involved, arsenic(III) is usually determined by oxidation with excess of dichromate and titration of the excess with iron(II).[8]

Spitalsky[9] first described the determination of chromate with arsenite solution, but the method has been little used because so many other simple methods exist. Later, Kolthoff and Sandell[10] applied the method to the rapid analysis of chromium-vanadium steels, but permanganate was used to determine the unreacted arsenic(III) and it is believed that in acid solution chromium(VI) is selectively reduced by arsenic(III) added to a mixture of chromium(VI) and vanadium(V). Szabó and Csányi[11] have made a determination of chromium(VI) by titrating directly with arsenic(III), using a catalyst mixture containing potassium iodide and manganese(II) sulphate, and diphenylamine as indicator; however the colour change towards the end of the titration seems to be slow, requiring a 5-min wait at the end-point to make sure that it has been reached. Swift[12] used an immiscible solvent as indicator for detecting the end-point in the titration of arsenic(III) with potassium dichromate, adding a small amount of iodine monochloride to the titration mixture before the start of the titration; this extended Andrews procedure requires the hydrochloric acid concentration not to fall below $8M$ near the end-point. The present communication describes experimental conditions for arsenic(III)-chromium(VI) titration with a sharp and reversible colour change at the end-point.

EXPERIMENTAL

Reagents

Arsenic(III) solution, approx. $0{\cdot}1N$. Prepared from analytical-reagent grade arsenious oxide, according to Vogel.[13]

Potassium dichromate, $0{\cdot}1N$.

Ferroin, 0·025 and $0{\cdot}01M$.

Hydroquinone, $0{\cdot}05N$. Prepared in $0{\cdot}5M$ sulphuric acid and standardized with ceric sulphate.[14]

Potassium ferrocyanide, $0{\cdot}05N$.

Uranium(IV), $0{\cdot}05N$. Prepared and standardized according to Kolthoff and Lingane.[15]

Molybdenum(V), 0·05M. Prepared by reduction in a mercury reductor and standardized according to Furman and Murray.[16]

Iodine monochloride. Add 25 ml of 0·04M potassium iodide and 40 ml of 12M hydrochloric acid to 20 ml of 0·025M potassium iodate. Add a few ml of chloroform and titrate with iodate or iodide, as needed, until a barely perceptible iodine colour remains in the organic solvent after shaking and settling. The aqueous phase is ~0·017M in iodine monochloride.

Iron(III) alum solution, approx. 10%, in 1M sulphuric acid. All other chemicals used in this investigation were of analytical-reagent grade.

Recommended procedures

Arsenic. To 4–10 ml of ~0·05N arsenic(III) solution, add 20 ml of iron(III) alum solution (~10%) and enough hydrochloric acid to make the titration solution 2·0–3·0M in hydrochloric acid near the equivalence point. Dilute to ~45 ml and add a drop or two of (~0·017M) iodine monochloride. Titrate with potassium dichromate, using a drop of 0·025M ferroin as indicator. The colour change at the end-point is from orange-red to intense greenish-yellow. An indicator correction of 0·02 ml of 0·05N dichromate is applied.

Hydroquinone (HQ). To 5–10 ml of ~0·05N HQ add 20 ml of ferric alum solution and make the mixture 1·5–3M in sulphuric acid or 1–2M in hydrochloric acid when diluted to ~45 ml. Add a drop of 0·01M ferroin and titrate with dichromate.

Ferrocyanide. The final ferricyanide concentration must be at least 0·005M. Titrate the ferrocyanide in the presence of 3N sulphuric or hydrochloric acid. The end-point is ~1·0% short of the equivalence point, so that it is essential to standardize the dichromate against ferrocyanide under the same conditions.

Uranium(IV) and molybdenum(V). Use the same conditions as for hydroquinone.

RESULTS AND DISCUSSION

Iodine monochloride is known to speed up the reduction of ferriin by arsenic(III) in dilute hydrochloric acid solution, but this catalytic effect diminishes with increasing concentration of hydrochloric acid. On the other hand, oxidation of ferroin by chromium(VI) is slow under similar experimental conditions but becomes rapid with increasing concentration of hydrochloric acid. With these opposing experimental conditions for rapid oxidation and reduction of the indicator, it has not proved possible to prescribe a working optimum condition for ferroin to serve as a satisfactory indicator, over the entire range of hydrochloric acid concentration studied (0·5–8·0M). At lower hydrochloric acid concentrations the equivalence point is overstepped and at higher concentrations the slow colour change of the indicator necessitates dropwise addition of titrant even at the beginning of the titration.

Iron(III) is reported to increase the speed of oxidation of ferroin by chromium(VI).[4] In ~0·08M iron(III) media this indicator reaction is fast enough, even in a solution which is only 2·0M in hydrochloric acid; the reduction of ferriin by arsenic(III) in the presence of a drop or two of iodine monochloride solution also being fast under the same experimental conditions, it is observed that the indicator works satisfactorily under such conditions. The behaviour of ferroin is completely satisfactory if the titration solution is 2·0–3·0M in hydrochloric acid, and can tolerate a further variation of 0·5M in the acid concentration (i.e., 1·5–3·5M), provided the titrant is added dropwise with a 30-sec wait between additions towards the close of titration. The titration is continued until the red colour of ferroin in the yellow of iron(III) chloride is completely discharged.

The reverse titration of chromium(VI) with arsenic(III) under similar experimental conditions is found to be equally satisfactory. The titration is continued until a permanent bright orange-red colour is obtained in the titration solution; the indicator correction is negligible. Typical results for both titrations are given in Table I.

Amounts of 250 mg of iron(III), 9 mg of chromium(III) and 295 mg of manganese(II) have been found not to interfere. Vanadium(IV), vanadium(V) and antimony(III) interfere in the titrations.

Kolthoff[17] prescribed an elevated temperature for dichromate titration of hydroquinone, presumably because of the sluggishness of the indicator reaction. The ferriin–HQ reaction is fast over a wide range of sulphuric acid concentration and the ferroin–Cr(VI) reaction becomes fast in 5M sulphuric acid. The titration is satisfactory in the latter medium if the temperature is not allowed to rise as a result of dilution of the acid, and the final quinone concentration is less than 0·002M. Use of iron(III) to catalyse the indicator reaction obviates the need to cool during the titration and permits the final quinone concentration to be up to 0·005M.

Ferricyanide catalyses the oxidation of the indicator, but ferrocyanide does not induce the oxidation as iron(II) does. It is not necessary to add iron(III) as catalyst.

TABLE 1

Amount of arsenic(III), *mmole*		Amount of chromium(VI), *mmole*	
taken	found	taken	found
0·1050	0·1052	0·06426	0·06436
0·1313	0·1316	0·07230	0·07240
0·1575	0·1574	0·08033	0·08028
0·1838	0·1835	0·08836	0·08845
0·2100	0·2104	0·09640	0·09636
0·2363	0·2368		
0·2625	0·2631		

Uranium(IV) and molybdenum(V) can both be titrated in 3–3·5*M* sulphuric acid. At lower acidities the indicator oxidation is slow, and at higher acidities (above 4*M* sulphuric acid for Mo) the ferroin colour is either prematurely discharged (in uranium titrations) or the reduction of ferriin is slow (molybdenum titrations). Molybdenum can be titrated in 4–5*M* hydrochloric acid, but the indicator reactions are too slow at other acidities. Uranium can be titrated in 3–4*M* hydrochloric acid. Chromium(VI) induces reduction of ferriin by uranium(IV) but the uranium does not induce oxidation of ferroin by chromium(VI). Iron(III) as catalyst permits use of a wider range of working conditions, *i.e.*, 1·5–3·5*M* sulphuric acid or 1–3*M* hydrochloric acid.

Department of Chemistry
Andhra University Postgraduate Centre
Guntur-5, Andhra Pradesh, India

K. SRIRAMAM

Summary—Working conditions for the titration of arsenic(III), hydroquinone, ferrocyanide, uranium(IV) and molybdenum(V) with dichromate in sulphuric acid and hydrochloric acid media have been established, with ferroin as the redox indicator.

Zusammenfassung—Es sind Arbeitsbedingungen für die Titrierung, mit Ferroin als Redoxanzeiger, von Arsen(III), Hydrochinon, Cyaneisen, Uranium(IV) und Molybdän(V) mit Bichromat in Schwefel- und Salzsäure Medium festgelegt worden.

Résumé—On a établi les conditions de travail pour le dosage des arsenic(III), hydroquinone, ferrocyanure, uranium(IV) et molybdène(V) avec le bichromate en milieux acide sulfurique et acide chlorhydrique, avec la ferroïne comme indicateur redox.

REFERENCES

1. I. M. Kolthoff and R. Belcher, *Volumetric Analysis, Vol. III*, Interscience, New York, 1957.
2. K. Sriramam, *Talanta*, 1971, **18**, 361.
3. G. F. Smith, *Anal. Chem.*, 1951, **23**, 925.
4. K. Sriramam, *Talanta*, 1972, **19**, 1085–1095.
5. K. Gleu, *Z. Anal. Chem.*, 1933, **95**, 305.
6. D. E. Metzler, R. J. Myers and E. H. Swift, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 625; H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1928, **50**, 1322; 1933, **55**, 3260; E. H. Swift and C. H. Gregory, *ibid.*, 1930, **52**, 901.
7. R. Lang and F. Kurtz, *Z. Anorg. Chem.*, 1929, **181**, 111; *cf.* R. Lang, and J. Zwerina, *ibid.*, 1928, **170**, 387, 289; R. Lang, *Z. Anal. Chem.*, 1935, **102**, 8.
8. W. J. Agnew, *Analyst*, 1943, **68**, 171; J. Knop, *Z. Anal. Chem.*, 1923, **63**, 96.
9. E. Spitalsky, *Z. Anorg. Chem.*, 1911, **69**, 179; *cf.* R. Lang, *ibid.*, 1926, **152**, 205; R. Lang and J. Zwerina, *Z. Elektrochem.*, 1928, **34**, 364; E. Zintl and P. Zaimis, *Z. Angew. Chem.*, 1927, **40**, 1286; 1928, **41**, 543.

10. I. M. Kolthoff, and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 140.
11. Z. G. Szabó and L. Csányi, *Anal. Chem.*, 1949, **21**, 1144.
12. E. H. Swift, *J. Am. Chem. Soc.*, 1930, **52**, 894.
13. A. I. Vogel, *Quantitative Inorganic Analysis*, 2nd Ed., Longmans, London, 1951.
14. I. M. Kolthoff and T. S. Lee, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 452.
15. I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 1933, **55**, 1871.
16. N. H. Furman and W. M. Murray, *ibid.*, 1936, **58**, 1689.
17. I. M. Kolthoff, *Rev. Trav. Chim.*, 1926, **45**, 745.

Talanta, 1972, Vol. 19, pp. 1448 to 1450. Pergamon Press. Printed in Northern Ireland

A note on successive complexometric determination of thorium and rare earths

(*Received* 2 *March* 1972. *Accepted* 25 *March* 1972)

IT IS WELL KNOWN[1] that in spite of a sufficient difference between the stability constants of the thorium–EDTA complex and the rare-earth complexes ($\log K_{\mathrm{ThY}} = 23{\cdot}2$, $\log K_{\mathrm{LaY}} = 15{\cdot}50$, $\log K_{\mathrm{DyY}} = 17{\cdot}9$), the rare earths (RE) cannot be titrated at pH 5–5·5 after thorium, when Xylenol Orange (XO), Pyrocatechol Violet, Methylthymol Blue *etc.* are used as indicators, because of the formation of coloured ternary complexes such as Th–EDTA–XO, at pH 4. EDTA does not saturate all the co-ordination sites of thorium. A few years ago we proposed[1] as titrants diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexaacetic acid (TTHA) for these successive titrations. DTPA and TTHA complexes of thorium do not react with Xylenol Orange (the best indicator for this purpose) at higher pH. Because of shortage of material at that time we studied only the first lanthanides, from lanthanum to neodymium. Later this procedure was extended to all RE by Mukherji.[2] Gupta and Powell[3] confirmed the original procedure and in addition for the titration of RE replaced DTPA by *N*-Hydroxyethylethylenediaminetriacetic acid (HEDTA). In all these procedures Xylenol Orange was used as indicator.

Because these volumetric reagents, especially TTHA and HEDTA, might not always be available, we have tried to improve the EDTA method. In principle the formation of the coloured Th–EDTA–XO complex has to be prevented by addition of another complex-forming compound. We have found that acetylacetone (acac) is very suitable for this reaction. We assume that the colourless ternary complex TH–EDTA–acac is formed instead of Th–EDTA–XO. This makes possible a reliable determination of RE after thorium titration. The whole procedure is very simple, as described below.

EXPERIMENTAL

Reagents

EDTA, 0·05*M*. Standardized with 0·05*M* lead nitrate, with Xylenol Orange as indicator. A 0·02*M* solution was made by appropriate dilution.

Rare earth solutions, 0·05*M*. Prepared by dissolving the nitrates in water or the oxides in nitric acid, and standardized by EDTA titration at pH 5–5·5, with Xylenol Orange as indicator.

Acetylacetone–acetone mixture (1:1).

Saturated hexamine solution.

Xylenol Orange solution, 0·5%.

Procedure

Dilute the sample solution, containing not more than 35 mg of thorium and 40–50 mg of RE, to 250–300 ml. Adjust the pH carefully to 2 ± 0·1, with sodium hydroxide or nitric acid. (Chloroacetic acid buffer is not suitable for thorium titration.) Add a few drops of Xylenol Orange indicator and titrate slowly with 0·02–0·05*M* EDTA to the colour change from the intense red colour to lemon yellow. Then warm the solution to 35–40°, add 20 ml of acetylacetone–acetone mixture and mix thoroughly (magnetic stirrer). Add saturated hexamine solution dropwise till an intensely red-violet colour appears and add a few drops of hexamine in excess. Titrate slowly with EDTA to a pure yellow or slightly orange-yellow. The amounts of EDTA used correspond to the thorium and the total RE respectively. Typical results are summarized in Table I.

10. I. M. Kolthoff, and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 140.
11. Z. G. Szabó and L. Csányi, *Anal. Chem.*, 1949, **21**, 1144.
12. E. H. Swift, *J. Am. Chem. Soc.*, 1930, **52**, 894.
13. A. I. Vogel, *Quantitative Inorganic Analysis*, 2nd Ed., Longmans, London, 1951.
14. I. M. Kolthoff and T. S. Lee, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 452.
15. I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 1933, **55**, 1871.
16. N. H. Furman and W. M. Murray, *ibid.*, 1936, **58**, 1689.
17. I. M. Kolthoff, *Rev. Trav. Chim.*, 1926, **45**, 745.

Talanta, 1972, Vol. 19, pp. 1448 to 1450. Pergamon Press. Printed in Northern Ireland

A note on successive complexometric determination of thorium and rare earths

(*Received* 2 *March* 1972. *Accepted* 25 *March* 1972)

IT IS WELL KNOWN[1] that in spite of a sufficient difference between the stability constants of the thorium–EDTA complex and the rare-earth complexes ($\log K_{\mathrm{ThY}} = 23{\cdot}2$, $\log K_{\mathrm{LaY}} = 15{\cdot}50$, $\log K_{\mathrm{DyY}} = 17{\cdot}9$), the rare earths (RE) cannot be titrated at pH 5–5·5 after thorium, when Xylenol Orange (XO), Pyrocatechol Violet, Methylthymol Blue *etc.* are used as indicators, because of the formation of coloured ternary complexes such as Th–EDTA–XO, at pH 4. EDTA does not saturate all the co-ordination sites of thorium. A few years ago we proposed[1] as titrants diethylenetriaminepenta-acetic acid (DTPA) and triethylenetetraminehexaacetic acid (TTHA) for these successive titrations. DTPA and TTHA complexes of thorium do not react with Xylenol Orange (the best indicator for this purpose) at higher pH. Because of shortage of material at that time we studied only the first lanthanides, from lanthanum to neodymium. Later this procedure was extended to all RE by Mukherji.[2] Gupta and Powell[3] confirmed the original procedure and in addition for the titration of RE replaced DTPA by *N*-Hydroxyethylethylenediaminetriacetic acid (HEDTA). In all these procedures Xylenol Orange was used as indicator.

Because these volumetric reagents, especially TTHA and HEDTA, might not always be available, we have tried to improve the EDTA method. In principle the formation of the coloured Th–EDTA–XO complex has to be prevented by addition of another complex-forming compound. We have found that acetylacetone (acac) is very suitable for this reaction. We assume that the colourless ternary complex TH–EDTA–acac is formed instead of Th–EDTA–XO. This makes possible a reliable determination of RE after thorium titration. The whole procedure is very simple, as described below.

EXPERIMENTAL

Reagents

EDTA, 0·05*M*. Standardized with 0·05*M* lead nitrate, with Xylenol Orange as indicator. A 0·02*M* solution was made by appropriate dilution.

Rare earth solutions, 0·05*M*. Prepared by dissolving the nitrates in water or the oxides in nitric acid, and standardized by EDTA titration at pH 5–5·5, with Xylenol Orange as indicator.

Acetylacetone–acetone mixture (1:1).

Saturated hexamine solution.

Xylenol Orange solution, 0·5%.

Procedure

Dilute the sample solution, containing not more than 35 mg of thorium and 40–50 mg of RE, to 250–300 ml. Adjust the pH carefully to 2 ± 0·1, with sodium hydroxide or nitric acid. (Chloroacetic acid buffer is not suitable for thorium titration.) Add a few drops of Xylenol Orange indicator and titrate slowly with 0·02–0·05*M* EDTA to the colour change from the intense red colour to lemon yellow. Then warm the solution to 35–40°, add 20 ml of acetylacetone–acetone mixture and mix thoroughly (magnetic stirrer). Add saturated hexamine solution dropwise till an intensely red-violet colour appears and add a few drops of hexamine in excess. Titrate slowly with EDTA to a pure yellow or slightly orange-yellow. The amounts of EDTA used correspond to the thorium and the total RE respectively. Typical results are summarized in Table I.

TABLE I.—DETERMINATION OF THORIUM AND RARE EARTHS.

Taken, *mg*		Found, *mg*		Difference, *mg*		Stability constants
Th	RE	Th	RE	Th	RE	$\log K_{ThY} - \log K_{REY}$
6·02	—	5·92*	—	−0·10	—	
12·04	—	12·06*	—	+0·02	—	
24·07	—	24·02*	—	−0·05	—	
36·11	—	36·08*	—	−0·03	—	
60·18	—	60·33†	—	+0·25	—	
12·04	7·44 La	11·95	7·43 La§	−0·09	−0·01	
12·04	37·20 La	11·95	36·26 La	−0·09	−0·94	
12·04	52·07 La	12·07	52·23 La	+0·03	+0·16	7·7
6·02	74·39 La	5·92	72·9–73 61 La	−0·10	−1·49–0·79	
6·02	35·91 Ce	5·92	36·43 Ce	−0·10	+0·52	
24·07	35·91 Ce	24·04	36·50 Ce	−0·03	+0·59	7·22
11·90	41·09 Sm	11·83	41·05 Sm	−0·07	−0·04	
35·71	4·11 Sm	35·62	4·20 Sm	−0·09	+0·09	6·10
5·95	34·49 Gd	6·26	34·67 Gd	+0·31	+0·18	5·83
11·90	7·62 Tb	11·95	7·71 Tb	+0·05	+0·09	5·30
11·90	38·09 Tb	12·41	38·54 Tb	+0·51	+0·45	
59·71	76·18 Tb	60·91‡	75·17 Tb	+1·20	−0·99	
5·95	38·95 Dy	5·92	39·16 Dy	−0·03	+0·21	4·9
41·66	3·90 Dy	41·65	4·06 Dy	−0·01	+0·16	
5·95	41·80 Er	8·70‡	39·64 Er	+1·75	−1·16	4·35
23·80	8·36 Er	24·02‡	8·11 Er	+0·22	−0·25	
11·90	37·35 Yb	23§‡	—	+11·10	—	3·70
35·71	3·74 Yb	37·01‡	2·88	+1·30	−0·86	

* After the titration, acac was added and pH adjusted with hexamine: no colour appeared.
† On addition of acac and adjustment of pH, slight formation of Th–EDTA–XO complex.
§ End-point from violet to pink not sharp. Insufficient amount of acac (see *Remarks*).
‡ Co-titration of RE, end-point sluggish and not sharp.

Remarks

The amount of thorium is limited to 35–40 mg in the volume stated. Higher concentrations of Th–EDTA complex need larger amounts of acac for suppressing the Th–EDTA–XO complex formation and this interferes with the subsequent titration of RE. Use of a higher temperature (40°) accelerates the dissolution of the acac–acetone mixture and makes the indicator colour change sharper.

Methylthymol Blue or Pyrocatechol Violet are not suitable for this procedure because of indistinct and sluggish end-points.

DISCUSSION

The proposed method is suitable for the determination of thorium and those rare earths having a sufficiently lower stability constant for their EDTA-complexes [lathanum up to erbium ($\log K_{ErY} = 18{\cdot}85$)]. Thulium ($\log K_{TmY} = 19{\cdot}51$) and lutetium ($\log K_{LuY} = 19{\cdot}83$) were not available, but we can assume that both will be partly co-titrated with thorium.

As an auxiliary complex-forming compound for RE titration, and masking of aluminium, iron, *etc*, Chernikhov *et al.*[4] proposed sulphosalicylic acid and titrated thorium with EDTA at pH 1·5 and then RE at pH 4·5, using Xylenol Orange as indicator. The method is limited to smaller amounts of thorium (up to 15 mg) and smaller amounts of RE. The colour change of Xylenol Orange is much less sharp than in the method described above.

Analytical Laboratory
J. Heyrovský Polarographic Institute
Czechoslovak Academy of Sciences
Prague 1, *Jilská* 16, *Czechoslovakia*

RUDOLF PŘIBIL
VLADIMÍR VESELÝ

Summary—An improved method for successive determination of thorium and rare earths is described. It is based on the EDTA titration of thorium at pH 2 (Xylenol Orange as indicator) followed by addition of acetylacetone–acetone mixture, adjustment of the pH to 5–5·5 with hexamine, and by further EDTA titration of rare earths with the same indicator.

Zusammenfassung—Ein verbessertes Verfahren zur Bestimmung von Thorium und seltenen Erden nacheinander wird beschrieben. Es beruht auf der EDTA-Titration von Thorium bei pH 2 (Indikator Xylenolorange), anschließender Zugabe eines Acetylaceton-Aceton-Gemisches, Einstellung des pH auf 5–5,5 mit Hexamethylentetramin und Weitertitration der seltenen Erden mit EDTA und dem selben Indikator.

Résumé—On décrit une méthode améliorée pour le dosage successif du thorium et des terres rares. Elle est basée sur le titrage à l'EDTA du thorium à pH 2 (Orangé Xylénol comme indicateur), suivi de l'addition d'un mélange acétylacétone-acétone, ajustement du pH à 5–5,5 par l'hexamine, et nouveau titrage à l'EDTA des terres rares avec le même indicateur.

REFERENCES

1. R. Přibil and V. Veselý, *Talanta*, 1962, **10**, 899.
2. A. K. Mukherji, *ibid.*, 1966, **13**, 1183.
3. A. K. Gupta and J. A. Powell, *ibid.*, 1964, **11**, 1339
4. Yu. A. Chernikhov, R. S. Tramm and K. S. Pevzner, *Zavodsk. Lab.*, 1960, **26**, 921; *Anal. Abstr.*, 1961, **8**, No. 1433.

Talanta, 1972, Vol. 19. pp. 1450 to 1454. Pergamon Press. Printed in Northern Ireland

Spectrophotometric study of the reaction of bismuth(III) with Xylenol Orange

(*Received* 16 *July* 1971. *Accepted* 16 *February* 1972)

Xylenol Orange forms complexes with bismuth(III), which can be used for spectrophotometric determination of bismuth.[1–8] It is generally believed that only the 1:1 Bi:XO complex is formed, but the system has not been fully studied. Our study shows that several complexes are formed.

EXPERIMENTAL

Reagents

Xylenol Orange solution $1{\cdot}00 \times 10^{-3}M$. The purity of the reagent was checked by elemental analysis.

Bismuth perchlorate solution $1{\cdot}00 \times 10^{-3}M$. Dissolve spectrally-pure metal in nitric acid, add perchloric acid and evaporate the solution. Dilute to volume (the pH should be ~1·3).

The pH of solutions was controlled with perchloric acid and sodium hydroxide. All investigations were carried out at a constant ionic strength of 1·0 maintained by the addition of the required amount of sodium perchlorate. The reagents used were *pro analysi* grade.

RESULTS AND DISCUSSION

The absorption spectra of bismuth(III) and Xylenol Orange (XO) solutions of various concentrations and pH are shown in Fig. 1. In acidic medium XO has an absorption maximum at 440 nm (curve 8). The addition of bismuth(III) gives rise to an absorption maximum at about 550 nm (curve 7). When XO is in excess in slightly acidic medium this maximum decreases and a new one appears at 500 nm (curves 1 and 6). These changes are associated with the formation of different complexes, the composition of which was established by the isomolar series and mole-ratio methods. The complex formed over the pH interval from −0·2 to 1·0 has a 1:1 composition, but the one formed at pH >1·0 has a 1:2 composition.

Summary—An improved method for successive determination of thorium and rare earths is described. It is based on the EDTA titration of thorium at pH 2 (Xylenol Orange as indicator) followed by addition of acetylacetone–acetone mixture, adjustment of the pH to 5–5·5 with hexamine, and by further EDTA titration of rare earths with the same indicator.

Zusammenfassung—Ein verbessertes Verfahren zur Bestimmung von Thorium und seltenen Erden nacheinander wird beschrieben. Es beruht auf der EDTA-Titration von Thorium bei pH 2 (Indikator Xylenolorange), anschließender Zugabe eines Acetylaceton-Aceton-Gemisches, Einstellung des pH auf 5–5,5 mit Hexamethylentetramin und Weitertitration der seltenen Erden mit EDTA und dem selben Indikator.

Résumé—On décrit une méthode améliorée pour le dosage successif du thorium et des terres rares. Elle est basée sur le titrage à l'EDTA du thorium à pH 2 (Orangé Xylénol comme indicateur), suivi de l'addition d'un mélange acétylacétone-acétone, ajustement du pH à 5–5,5 par l'hexamine, et nouveau titrage à l'EDTA des terres rares avec le même indicateur.

REFERENCES

1. R. Přibil and V. Veselý, *Talanta*, 1962, **10**, 899.
2. A. K. Mukherji, *ibid.*, 1966, **13**, 1183.
3. A. K. Gupta and J. A. Powell, *ibid.*, 1964, **11**, 1339
4. Yu. A. Chernikhov, R. S. Tramm and K. S. Pevzner, *Zavodsk. Lab.*, 1960, **26**, 921; *Anal. Abstr.*, 1961, **8**, No. 1433.

Talanta, 1972, Vol. 19. pp. 1450 to 1454. Pergamon Press. Printed in Northern Ireland

Spectrophotometric study of the reaction of bismuth(III) with Xylenol Orange

(*Received* 16 *July* 1971. *Accepted* 16 *February* 1972)

XYLENOL ORANGE forms complexes with bismuth(III), which can be used for spectrophotometric determination of bismuth.[1–8] It is generally believed that only the 1:1 Bi:XO complex is formed, but the system has not been fully studied. Our study shows that several complexes are formed.

EXPERIMENTAL

Reagents

Xylenol Orange solution $1{\cdot}00 \times 10^{-3}M$. The purity of the reagent was checked by elemental analysis.

Bismuth perchlorate solution $1{\cdot}00 \times 10^{-3}M$. Dissolve spectrally-pure metal in nitric acid, add perchloric acid and evaporate the solution. Dilute to volume (the pH should be ~1·3).

The pH of solutions was controlled with perchloric acid and sodium hydroxide. All investigations were carried out at a constant ionic strength of 1·0 maintained by the addition of the required amount of sodium perchlorate. The reagents used were *pro analysi* grade.

RESULTS AND DISCUSSION

The absorption spectra of bismuth(III) and Xylenol Orange (XO) solutions of various concentrations and pH are shown in Fig. 1. In acidic medium XO has an absorption maximum at 440 nm (curve 8). The addition of bismuth(III) gives rise to an absorption maximum at about 550 nm (curve 7). When XO is in excess in slightly acidic medium this maximum decreases and a new one appears at 500 nm (curves 1 and 6). These changes are associated with the formation of different complexes, the composition of which was established by the isomolar series and mole-ratio methods. The complex formed over the pH interval from −0·2 to 1·0 has a 1:1 composition, but the one formed at pH >1·0 has a 1:2 composition.

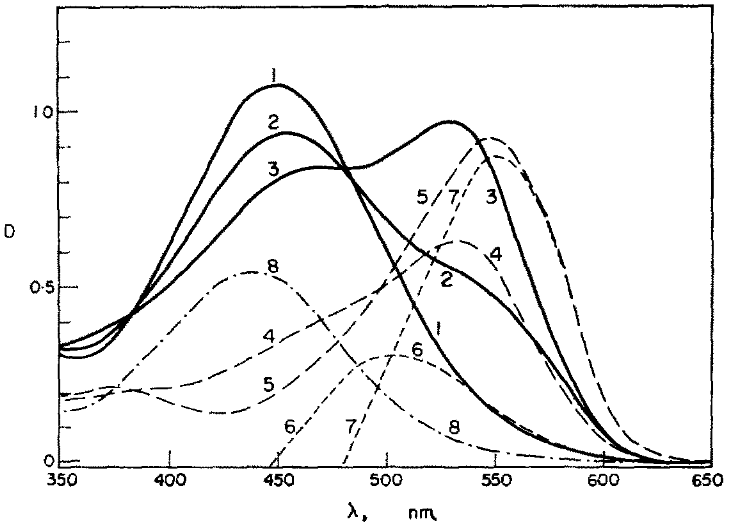


FIG. 1.—Absorption spectra
1–3, $C_{Bi} = 4{\cdot}00 \times 10^{-5}M$, $C_{XO} = 8{\cdot}00 \times 10^{-5}M$; *1*, pH = 4·0; *2*, pH = 2·0; *3*, pH = 0·8.
4–5, $C_{Bi} = 2{\cdot}00 \times 10^{-4}M$, $C_{XO} = 4{\cdot}00 \times 10^{-5}M$; *4*, pH = 0·4; *5*, pH = 1·0.
6, $C_{Bi} = 4{\cdot}00 \times 10^{-5}M$; $C_{XO} = 2{\cdot}00 \times 10^{-4}M$, pH = 3·0.
7, $C_{Bi} = 2{\cdot}00 \times 10^{-4}M$; $C_{XO} = 4{\cdot}00 \times 10^{-5}M$, pH = 1·0.
8, $C_{XO} = 4{\cdot}00 \times 10^{-5}M$, pH = 1·8.
1–5 and *8*, water blank; *6* and *7*, XO blank.

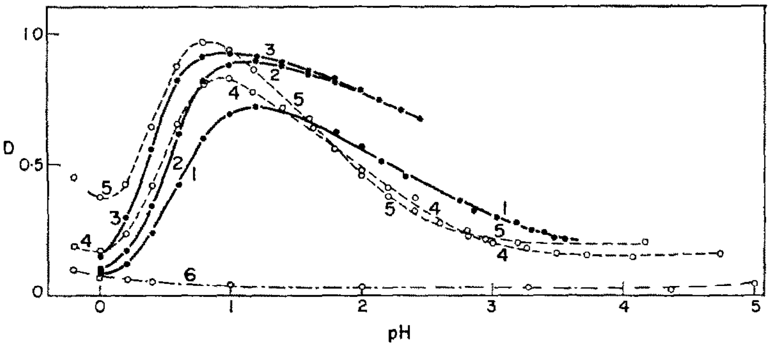


FIG. 2.—Absorbance as a function of pH, at 550 nm
C_{Bi}: *1*, $4{\cdot}00 \times 10^{-5}M$; *2*, $8{\cdot}00 \times 10^{-5}M$; *3*, $2{\cdot}00 \times 10^{-4}M$; *4* and *5*, $4{\cdot}00 \times 10^{-5}M$.
C_{XO}: *1*, *2* and *3*, $4{\cdot}00 \times 10^{-5}M$; *4*, $8{\cdot}00 \times 10^{-5}M$; *5*, $2{\cdot}00 \times 10^{-4}M$; *6*, $4{\cdot}00 \times 10^{-5}M$. XO blank.

pH–absorbance curves of various mixtures of bismuth(III) and XO (Fig. 2) have been used to determine the composition and dissociation constants of the complexes.

The dissociation constants of Xylenol Orange[10] and those of the hydroxo-complexes of Bi(III),[11] suggest that the formation of the complex in the pH range from −0·2 to 1 can be expressed by

$$\mathrm{Bi(OH)}_{3-i}^{i+} + \mathrm{H}_m\mathrm{R}^{(m-6)+} \rightleftharpoons [\mathrm{Bi(OH)}_{3-i}\mathrm{H}_{m-n}\mathrm{R}]^{(i+m-6-n)+} + n\mathrm{H}^+ \qquad (1)$$

The number of hydrogen ions (n) involved was determined by using the dependence of $-\log A$ on pH:

$$A = \frac{[\mathrm{Bi(OH)}_{3-i}][\mathrm{H}_m\mathrm{R}]}{[\mathrm{Bi(OH)}_{3-i}\mathrm{H}_{m-n}\mathrm{R}]} = \frac{C_{\mathrm{Bi}}(D_{\max} - D') \cdot (aD_{\max} - D')}{D_{\max} \cdot D' \cdot f_{\mathrm{Bi(OH)}_{3-i}} \cdot f_{\mathrm{H_6R}}} \qquad (2)$$

where D_{max} is the maximum absorbance at pH 0·8–1·0 when the concentration of XO is constant ($C_{XO} = 4{\cdot}00 \times 10^{-5}M$) and the ratio [Bi]/[XO] is greater than 2, C_{Bi} and C_{XO} are the total analytical concentrations of Bi and XO, $a = C_{Bi}/C_{XO}$ when Bi(III) is in excess and C_{XO}/C_{Bi} when XO is in excess, $f_{H_6R} = C_{XO}/[H_6R]$, $f_{Bi(OH)_{3-i}} = C_{Bi}/[Bi(OH)_{3-i}]$. The absorbance D' of the mixture at 550 nm has a contribution from XO which must be allowed for.

The plot of $-\log A$ against pH is a straight line with slope $n = 3$. Consequently, the complex has the composition $[Bi(H_3R)]$. It is possible to calculate its dissociation constant from the values of A by using the equation:

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} = \frac{A \cdot f_{H_6R}}{f_{H_3R}} \tag{3}$$

The values of this constant have been calculated from curves 1–5 in Fig. 2. After a statistical treatment of the results the value of $pK_{Bi(H_3R)}$ is found to be 9·80 ± 0·03.

The formation of the 1:2 complex can be expressed by

$$Bi(H_3R) + H_mR^{(m-6)+} \rightleftharpoons [Bi(H_{m+3-n}R_2)]^{(m-6-n)+} + nH^+ \tag{4}$$

In the interval from pH 1·0 to 3·0, where the 1:1 complex is changed into the 1:2 complex H_5R^- begins to predominate.

The dependence of log B against pH has been used to determine the number of hydrogen ions involved in reaction (4):

$$B = \frac{[Bi(H_{8-n}R_2)]}{[Bi(H_3R)]} \cdot f_{H_5R} = \left(\frac{D_{max} - D'}{D' - D_{min}}\right) f_{H_5R} \tag{5}$$

where D_{min} is the minimum absorbance at pH > 3·0 when the concentration of Bi(III) is constant ($C_{Bi} = 4{\cdot}00 \times 10^{-5}M$) and $C_{XO}/C_{Bi} > 2$.

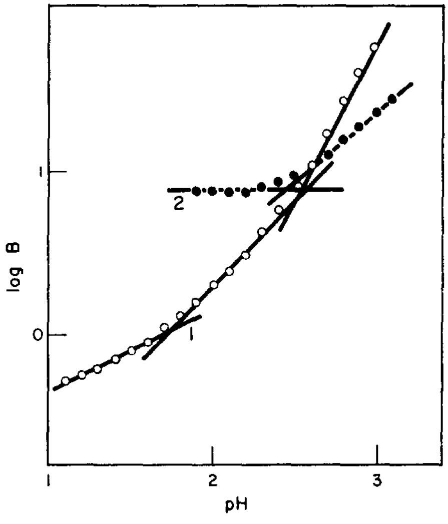


FIG. 3.—Dependence of log B on pH at 550 nm, $D_{min} = 0{\cdot}133$.
1, $C_{Bi} = 4{\cdot}00 \times 10^{-5}M$; $C_{XO} = 8{\cdot}00 \times 10^{-5}M$.
2, $C_{Bi} = 4{\cdot}00 \times 10^{-5}M$; $C_{XO} = 2{\cdot}00 \times 10^{-4}M$.

The number of protons released varies with pH (Fig. 3, curve 1). It is evident that with the increase of pH, bismuth(III) forms complexes with various ionic groups on XO.

pH 1·0–1·7 $n = 0{\cdot}5$

$$2Bi(H_3R) + 2H_5R^- \rightleftharpoons [Bi(H_4R)_2]^- + [Bi(H_4R)(H_3R)]^{2-} + H^+ \tag{6}$$

pH 1·7–2·4 $n = 1$

$$Bi(H_3R) + H_5R^- \rightleftharpoons [Bi(H_4R)(H_3R)]^{2-} + H^+ \tag{7}$$

pH > 2·4 $n = 2$

$$Bi(H_3R) + H_5R^- \rightleftharpoons [Bi(H_3R)_2]^{3-} + 2H^+ \tag{8}$$

As H_5R^- and H_4R^{2-} co-exist, the number of hydrogen ions involved can be determined if H_4R^{2-} takes part in the reaction between bismuth(III) and XO (Fig. 3, curve 2). The result for n also confirms the conclusion about the composition of the complex compounds.

$pH < 2{\cdot}4 \quad n = 0$

$$Bi(H_3R) + H_4R^{2-} \rightleftharpoons [Bi(H_4R)(H_3R)]^{2-} \tag{9}$$

$pH > 2{\cdot}4 \quad n = 1$

$$Bi(H_3R) + H_4R^{2-} \rightleftharpoons [Bi(H_3R)_2]^{3-} + H^+ \tag{10}$$

It is seen that from curves 4 and 5 in Fig. 2 that at pH > 3·0 bismuth(III) is completely bound as $[Bi(H_3R)_2]^{3-}$. This enables its dissociation constant to be calculated from the equation

$$K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}} = \frac{K_{Bi(H_3R)} \cdot C_{XO} \cdot f_{H_5R}}{B \cdot f_{H_3R}} \tag{11}$$

The value of $pK_{Bi(H_3R)_2}$ is 15·53 ± 0·03.

Department of Analytical Chemistry
Higher Institute of Chemical Technology and Metallurgy
Sofia-56, Bulgaria

DONKA KANTCHEVA
PETRANA NENOVA
BORISLAV KARADAKOV

Summary—The reaction between bismuth(III) and Xylenol Orange (XO) has been investigated by spectrophotometry. It has been established that bismuth(III) and Xylenol Orange form complex compounds with compositions Bi(III):XO = 1:1 (up to pH 1) and Bi(III):XO = 1:2 (above pH 1) which have absorption maxima at 550 and 500 nm respectively. The formula of the 1:1 complex is $[Bi(H_3R)]$ whereas the 1:2 complex can take one of the following forms: $[Bi(H_4R)_2]^{1-}$, $[Bi(H_4R)(H_3R)]^{2-}$ and $[Bi(H_3R)_2]^{3-}$.
If

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} \quad \text{and} \quad K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}}$$

the values for $pK_{Bi(H_3R)}$ and $pK_{Bi(H_3R)_2}$ respectively are 9·80 ± 0·03 and 15·53 ± 0·03 at a constant ionic strength of 1·0.

Zusammenfassung—Die Reaktion zwischen Wismuth(III) und Xylenol Orange (XO) ist mit Spektralphotometrie untersucht worden. Es ist festgestellt worden, dass Wismuth(III) und Xylenol Orange Komplexverbindungen mit Bi(III):XO = 1:1 (bis zu pHl) Verbindungen und Bi(III):XO = 1:2 (über pHl) bilden, welche Absorptionsmaximums von 550 bzw. 500 nm haben. Die Formel der 1:1 Komplexverbindung ist $[Bi(H_3R)]$, während die 1:2 Komplexverbindung eine der folgenden Formen annehmen kann: $[Bi(H_4R)_2]$, $[Bi(H_4R)(H_3R)^{2-}$ und $[Bi(H_3R)]^{3-}$.
Wenn

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} \quad \text{und} \quad K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}}$$

sind die Werte für $pK_{Bi(H_3R)}$ bzw. $pK_{Bi(H_3R)_2}$ 9,80 ± 0,03 und 15,53 ± 0,03 bei konstanter Ionenstärke von 1,0.

Résumé—On a étudié par spectrophotométrie la réaction entre le bismuth(III) et l'Orangé Xylénol (XO). On a établi que le bismuth(III) et l'Orangé Xylénol forment des composés complexes de compositions Bi(III):XO = 1:1 (jusqu'à pH 1) et Bi(III):XO = 1:2 (au-dessus de pH 1), qui ont des maximums d'absorption à 550 et 500 nm respectivement. La formule du complexe 1:1 est $[Bi(H_3R)]$, tandis que le complexe 1:2 peut prendre l'une des formes suivantes: $[Bi(H_4R)_2]$, $[Bi(H_4R)(H_3R)]^{2-}$ et $[Bi(H_3R)_2]^{3-}$.

Si

$$K_{\mathrm{Bi(H_3R)}} = \frac{[\mathrm{Bi^{3+}}][\mathrm{H_3R^{3-}}]}{[\mathrm{Bi(H_3R)}]} \quad \text{et} \quad K_{\mathrm{Bi(H_3R)_2}} = \frac{[\mathrm{Bi^{3+}}][\mathrm{H_3R^{3-}}]^2}{[\mathrm{Bi(H_3R)_2}]^{3-}}$$

les valeurs pour $\mathrm{p}K_{\mathrm{Bi(H_3R)}}$ et $\mathrm{p}K_{\mathrm{Bi(H_3R)_2}}$ sont respectivement 9,80 ± 0,03 et 15,53 ± 0,03 à une force ionique constante de 1,0.

REFERENCES

1. K. L. Cheng, *Talanta*, 1960, **5**, 254.
2. H. Onishi and N. Ishiwatari, *Bull. Chem. Soc. Japan*, 1960, **33**, 1581.
3. *Idem*, *Talanta*, 1961, **8**, 753.
4. V. N. Danillova and P. V. Marchenko, *Zavodsk. Lab.*, 1962, **28**, 654.
5. A. A. Amsheeva and D. V. Bezugly, *Zh. Analit. Khim.*, 1964, **19**, 97.
6. K. N. Bagdassarov, P. N. Kovallenko and M. A. Shemakina, *ibid.*, 1968, **23**, 515.
7. P. N. Kovallenko, K. N. Bagdassarov, O. E. Shellepin and M. A. Shemakina, *Zh. Neorgan. Khim.*, 1968, **38**, 2015.
8. I. Adamiec, *Chem. Anal. (Warsaw)*, 1968, **13**, 147.
9. R. Přibil, *Talanta*, 1959, **3**, 200.
10. B. Řehák and J. Körbl, *Collection Czech. Chem. Commun.*, 1960, **25**, 797.
11. U. U. Lurre, *Handbook of Analytical Chemistry*, Moscow, 1965.

Talanta, 1972, Vol. 19, pp. 1454 to 1457. Pergamon Press. Printed in Northern Ireland

Radiochemical separation of zirconium and hafnium from other radionuclides

(*Received* 17 *February* 1972. *Accepted* 3 *March* 1972)

NEUTRON-ACTIVATION techniques have been used for the determination of zirconium and/or hafnium in a variety of materials.[1,2] Most methods employ thermal neutrons and relatively long radiation periods to form ^{181}Hf ($t_{1/2}$ = 42·5 d) and ^{95}Zr ($t_{1/2}$ = 65·5 d). After a suitable cooling period for the decay of short-lived activities, zirconium and hafnium are separated from other activities and gamma-counted (usually the 0·482-MeV gamma-ray for Hf and the 0·722 + 0·754 MeV gamma-rays for Zr). The method is quite sensitive for hafnium owing to its relatively high cross-section but is less sensitive for zirconium. Koch[2] gives sensitivities of 40 pg for hafnium and 6 ng for zirconium. Because of interferences from other gamma-emitters, a radio-chemical separation is usually necessary before counting.

Many methods have been recommended for the separation of zirconium and hafnium from other radionuclides.[3] Most of them are lenthy and tedious. A recent method devised by Brooks[4] utilizes precipitation with mandelic acid, a highly selective reagent for zirconium and hafnium[5,6] for separation from all activities except those of ^{46}Sc and ^{233}Pa. Solvent extraction with cupferron in chloroform separated zirconium and hafnium from scandium, and the protactinium was removed by scavenging with niobium pentoxide in acid solution. The mandelic acid precipitate was ignited to the oxide for weighing and counting.

The method proposed in this paper represents an improvement over Brook's method since it eliminates the solvent extraction step and removes both protactinium and scandium simultaneously in a single, simple scavenging operation in which the precipitate is dissolved in sodium carbonate solution[7] and barium carbonate subsequently precipitated. Ignition to the oxide is also eliminated since zirconium and hafnium tetramandelate may be weighed directly.[8]

EXPERIMENTAL

Reagents

Zirconium standard (1·00 mg/ml). A known weight of "Specpure" $ZrOCl_2 \cdot 8H_2O$ (Johnson, Matthey and Co.) was dissolved in a known volume of 1*N* sulphuric acid prepared with distilled demineralized water, and the solution standardized gravimetrically by the mandelic acid and cupferron methods. Standard solutions could be made with an error of ±3·0% by direct weighing of the $ZrOCl_2 \cdot 8H_2O$ (3·533 mg of $ZrOCl_2 \cdot 8H_2O$ is equivalent to 1·000 mg of Zr).

Hafnium standard (1·00 mg/ml). Similarly prepared (from "Specpure" $HfOCl_2 \cdot 8H_2O$) and standardized. Preparation by direct weighing (2·294 mg of $HfOCl_2 \cdot 8H_2O$ is equivalent to 1·000 mg of Hf) again gave ±3·0% error.

Si

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} \quad \text{et} \quad K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}}$$

les valeurs pour $pK_{Bi(H_3R)}$ et $pK_{Bi(H_3R)_2}$ sont respectivement 9,80 ± 0,03 et 15,53 ± 0,03 à une force ionique constante de 1,0.

REFERENCES

1. K. L. Cheng, *Talanta*, 1960, **5**, 254.
2. H. Onishi and N. Ishiwatari, *Bull. Chem. Soc. Japan*, 1960, **33**, 1581.
3. *Idem*, *Talanta*, 1961, **8**, 753.
4. V. N. Danillova and P. V. Marchenko, *Zavodsk. Lab.*, 1962, **28**, 654.
5. A. A. Amsheeva and D. V. Bezugly, *Zh. Analit. Khim.*, 1964, **19**, 97.
6. K. N. Bagdassarov, P. N. Kovallenko and M. A. Shemakina, *ibid.*, 1968, **23**, 515.
7. P. N. Kovallenko, K. N. Bagdassarov, O. E. Shellepin and M. A. Shemakina, *Zh. Neorgan. Khim.*, 1968, **38**, 2015.
8. I. Adamiec, *Chem. Anal. (Warsaw)*, 1968, **13**, 147.
9. R. Přibil, *Talanta*, 1959, **3**, 200.
10. B. Řehák and J. Körbl, *Collection Czech. Chem. Commun.*, 1960, **25**, 797.
11. U. U. Lurre, *Handbook of Analytical Chemistry*, Moscow, 1965.

Talanta, 1972, Vol. 19, pp. 1454 to 1457. Pergamon Press. Printed in Northern Ireland

Radiochemical separation of zirconium and hafnium from other radionuclides

(*Received* 17 *February* 1972. *Accepted* 3 *March* 1972)

NEUTRON-ACTIVATION techniques have been used for the determination of zirconium and/or hafnium in a variety of materials.[1,2] Most methods employ thermal neutrons and relatively long radiation periods to form ^{181}Hf ($t_{1/2}$ = 42·5 d) and ^{95}Zr ($t_{1/2}$ = 65·5 d). After a suitable cooling period for the decay of short-lived activities, zirconium and hafnium are separated from other activities and gamma-counted (usually the 0·482-MeV gamma-ray for Hf and the 0·722 + 0·754 MeV gamma-rays for Zr). The method is quite sensitive for hafnium owing to its relatively high cross-section but is less sensitive for zirconium. Koch[2] gives sensitivities of 40 pg for hafnium and 6 ng for zirconium. Because of interferences from other gamma-emitters, a radio-chemical separation is usually necessary before counting.

Many methods have been recommended for the separation of zirconium and hafnium from other radionuclides.[3] Most of them are lenthy and tedious. A recent method devised by Brooks[4] utilizes precipitation with mandelic acid, a highly selective reagent for zirconium and hafnium[5,6] for separation from all activities except those of ^{46}Sc and ^{233}Pa. Solvent extraction with cupferron in chloroform separated zirconium and hafnium from scandium, and the protactinium was removed by scavenging with niobium pentoxide in acid solution. The mandelic acid precipitate was ignited to the oxide for weighing and counting.

The method proposed in this paper represents an improvement over Brook's method since it eliminates the solvent extraction step and removes both protactinium and scandium simultaneously in a single, simple scavenging operation in which the precipitate is dissolved in sodium carbonate solution[7] and barium carbonate subsequently precipitated. Ignition to the oxide is also eliminated since zirconium and hafnium tetramandelate may be weighed directly.[8]

EXPERIMENTAL

Reagents

Zirconium standard (1·00 mg/ml). A known weight of "Specpure" $ZrOCl_2 \cdot 8H_2O$ (Johnson, Matthey and Co.) was dissolved in a known volume of 1*N* sulphuric acid prepared with distilled demineralized water, and the solution standardized gravimetrically by the mandelic acid and cupferron methods. Standard solutions could be made with an error of ±3·0% by direct weighing of the $ZrOCl_2 \cdot 8H_2O$ (3·533 mg of $ZrOCl_2 \cdot 8H_2O$ is equivalent to 1·000 mg of Zr).

Hafnium standard (1·00 mg/ml). Similarly prepared (from "Specpure" $HfOCl_2 \cdot 8H_2O$) and standardized. Preparation by direct weighing (2·294 mg of $HfOCl_2 \cdot 8H_2O$ is equivalent to 1·000 mg of Hf) again gave ±3·0% error.

Zirconium carrier (*approx.* 10 mg/ml). Prepared by dissolving commercial zirconyl chloride in $1M$ hydrochloric acid, heating and filtering. Standardized by precipitating zirconium mandelate as in steps 1–4 of the procedure, collecting on a sintered-glass filter with the aid of 95% ethyl alcohol or acetone, drying at 110–120° for 1 hr, cooling and weighing.

Mandelic acid solution, 15% w/v.

Barium nitrate solution, 2% w/v.

Procedure

(1) Place 1 ml of zirconyl chloride carrier in a 40-ml centrifuge tube, then add a measured amount of the sample to be analysed. The sample should be in hydrochloric acid solution. Fluorides, phosphates, oxalates, nitrates, and strong oxidizing agents should be absent since they interfere in the precipitation of zirconium tetramandelate. Adjust the volume to approximately 15–20 ml and the concentration of hydrochloric acid to $5–10M$.

(2) Heat to at least 90° in a boiling water-bath, then add 10 ml of mandelic acid solution. Stir thoroughly, continue heating with occasional stirring until the precipitate has completely settled (approx. 30 min), then remove the tube and let stand until cool (about 30 min).

(3) Centrifuge, discard the supernatant liquid, stir the precipitate with 5 ml of 2% mandelic acid solution in $4M$ hydrochloric acid, centrifuge, and discard the washings.

(4) Stir the precipitate with 10 ml of distilled water, wash the stirring rod and sides of the tube with about 1 ml of 95% ethyl alcohol to wet any floating hydrophobic precipitate. Centrifuge and discard the washings.

(5) Add 3 ml of $1M$ sodium carbonate solution and stir to dissolve the precipitate. Do not heat the mixture to hasten dissolution, as this will decompose the soluble carbonato-complexes of zirconium and hafnium.

(6) Wash down the sides of the tube with about 2 ml of distilled water, then add 1 ml of barium nitrate solution *dropwise and with vigorous stirring* (otherwise scavenging is less effective). Centrifuge, and decant the supernatant solution into a clean tube.

(7) Cautiously add six 1-ml portions of conc. hydrochloric acid, allowing effervescence to subside between additions. Cautiously stir to expel carbon dioxide, then place the tubes in a boiling water-bath for 5–10 min, stirring vigorously from time to time to eliminate all carbon dioxide.

(8) Repeat steps 2–7, then proceed to step 9.

(9) Add 10 ml of distilled water to the precipitate, stir vigorously, then wash down the stirring rod and the sides of the tube with about 1 ml of 95% ethyl alcohol. Centrifuge and discard the washings.

(10) Add 10 ml of 95% ethyl alcohol and stir vigorously. Centrifuge and discard the washings.

(11) Transfer the precipitate to a tared planchet with about 1 ml of 95% ethyl alcohol. Dry for 15–30 min under an infrared lamp or in an oven at 110–120°. Let cool, weigh, and count. If the gamma spectrum indicates contamination, the dried sample may be dissolved in sodium carbonate and the procedure repeated, starting with step 5.

DISCUSSION

Choice of carrier

Tracer experiments with ^{95}Zr and ^{181}Hf and with pure hafnyl and zirconyl chlorides as carrier demonstrated quantitative recoveries of both radionuclides. Commercial zirconyl chloride was chosen as carrier since it also contains hafnium (about 2%) and trace impurities such as rare earths, *etc*, which would function as holdback carriers. With two scavenging steps, excellent carrier recoveries were obtained, ranging from 80 to 90%

Separations

Studies with various tracers confirmed Brook's observations that precipitation of zirconium mandelate separates zirconium and hafnium activities from all radionuclides except protactinium and scandium. Without scavenging, approximately 10–20% of the two latter activities were carried down with the zirconium. After scavenging, no detectable protactinium activity remained, but about 10^{-3}% of the original scandium activity remained.

Testing the method

The method was checked by analysing a dilute solution of commercial zirconyl chloride for both zirconium and hafnium, and by analysing the standard rock samples G-1 and W-1. Samples and standards were weighed into silica ampoules, sealed, then irradiated in a reactor with a thermal neutron flux of 5 × 10^{12} n/cm^2/sec for a period of either one or two weeks. After a cooling period of about two weeks the samples were dissolved and analysed.

Measurements were made with a 30-cm^3 co-axial Ge(Li) detector coupled to a 2000-channel PDB-8/gamma-spectrometer system. Excellent resolution was attained and both photopeaks of zirconium, at 0·722 and 0·754 MeV were clearly resolved. The 0·722-MeV peak was used for zirconium and the 0·482-MeV peak for hafnium. Results are compiled in Tables I and II.

TABLE I.—ANALYSIS OF COMMERICAL ZIRCONYL CHLORIDE.

Sample	Zr found, *µg*	Hf found, *µg*	Hafnium, %	Total Zr + Hf taken, *µg*	Total Zr + Hf found, *µg*
1	10·9	0·22	2·0	11·9	11·1
2	20·1	0·40	2·0	20·2	20·5

(Irradiation for 1 week)

Discussion of results

No analyses were available for the commercial zirconyl chloride. The results must be judged from the precision of the hafnium determinations and from the total zirconium plus hafnium recovered, compared with that taken.

TABLE II.—DETERMINATION OF ZIRCONIUM AND HAFNIUM IN STANDARD ROCK SAMPLES.

Sample*		Zr, *ppm* Found	Zr, *ppm* Recommended value	Hf, *ppm* Found	Hf, *ppm* Recommended value
G-1	(*a*)	231	210	6·0	6
	(*b*)	201	210	5·8	6
W-1	(*a*)	103	100	2·6	2
	(*b*)	107	100	2·3	2

* Irradiated for (*a*) 1 week, (*b*) 2 weeks.

About 100 mg of standard rock were fused with a mixture of sodium hydroxide and sodium peroxide in nickel crucibles, by the procedure recommended by Brooks.[4] Carrier was added before fusion by adding 1·0 ml of zirconyl chloride carrier to an excess of 6*M* ammonia solution in the crucible, and evaporating to dryness. After fusion the cake was treated with water and digested at 90° for about 30 min to ensure complete removal from the crucible. The residue was centrifuged down and the alkaline supernatant liquid discarded. The residue was washed once with hot water, then dissolved by heating with 15 ml of conc. hydrochloric acid. This solution was used for the zirconium and hafnium determinations.

Duplicate analyses given in Tables I and II are results from separate irradiations using new, different standards, to eliminate systematic errors arising from the preparation of standard and from the irradiation.

Acknowledgements—The author wishes to thank Dr. A. A. Smales, Mr. David Mapper, and Mr. Peter Kay for their advice and assistance and also the United Kingdom Atomic Energy Research Establishment for providing equipment and facilities for this research.

Analytical Sciences Division
U.K. Atomic Energy Research Establishment
Harwell, Berks., U.K.

RICHARD B. HAHN*

* Visiting Scientist, present address: Chemistry Department, Wayne State University, Detroit, Michigan 48202, U.S.A.

Summary—Radiozirconium and radiohafnium may be separated from all other radionuclides except scandium and protactinium by precipitation with mandelic acid from 5–10*M* hydrochloric acid, using commercial zirconyl chloride as carrier. Scandium and protactinium are removed by dissolving the precipitate in sodium carbonate, then adding barium nitrate to precipitate barium carbonate which acts as a scavenger. Zirconium mandelate is finally reprecipitated and the sample weighed and counted in this form. The method was checked by analysing commercial zirconyl chloride and standard rock samples for zirconium and hafnium by neutron-activation analysis.

Zusammenfassung—Radiozirkonium und Radiohafnium kann von allen anderen Radionukliden ausser Scandium und Protaktinium durch Niederschlag mit Mandelsäure aus 5–10*M* Salzsäure mittels handelsüblichem Zirkoniumchlorid als Träger getrennt werden. Scandium und Protaktinium werden durch Auflösen des Niederschlags in Natriumkarbonat und dann Zufügung von Bariumnitrat zum Niederschlagen von Bariumkarbonat entfernt, welch letzteres als Spülmittel fungiert. Zirkoniummandelat wird schliesslich wieder niedergeschlagen, und das Muster wird gewogen und in dieser Form berechnet. Das Verfahren wurde durch Analysieren von gewerblichem Zirkoniumchlorid und normalen Gesteinmustern von Zirkonium und Hafnium mittels Neutronaktivierungsanalyse geprüft.

Résumé—On peut séparer le radiozirconium et le radiohafnium de tous les autres radionuclides à l'exception du scandium et du protactinium par précipitation avec l'acide mandélique à partir d'acide chlorhydrique 5–10*M*, en utilisant le chlorure de zirconyle commercial comme entraîneur. On élimine le scandium et le protactinium en dissolvant le précipité dans du carbonate de sodium, puis en ajoutant du nitrate de baryum pour précipiter le carbonate de baryum qui agit comme un fixateur. Le mandélate de zirconium est finalement reprécipité et l'échantillon est pesé et compté sous cette forme. On a contrôlé la méthode en analysant le chlorure de zirconyle commercial et des échantillons de roche étalon pour le zirconium et le hafnium par analyse par activation de neutrons.

REFERENCES

1. W. S. Lyon, *Guide to Activation Analysis*, Van Nostrand, Princeton, 1964.
2. R. C. Koch, *Activation Analysis Handbook*, Academic Press, New York, 1960.
3. E. P. Steinberg, *The Radiochemistry of Zirconium and Hafnium*, National Nuclear Energy Series, NAS-NS 3011, Office of Technical Services, Washington, D.C. 1960.
4. C. K. Brooks, *Radiochimica Acta*, 1968, **8**, 167
5. C. A. Kumins, *Anal. Chem.*, 1947, **19**, 376.
6. R. B. Hahn, *ibid.*, 1951, **23**, 1259.
7. R. B. Hahn and L. Weber, *J. Am. Chem. Soc.*, 1955, **77**, 4777.
8. R. B. Hahn and E. S. Baginski, *Anal. Chim. Acta*, 1956, **14**, 45.

Talanta 1972. Vol. 19, pp. 1457 to 1460. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in phosphazenes and phosphines*

(*Received* 24 *April* 1972. *Accepted* 1 *May* 1972)

IN RECENT YEARS organic polymers have grown in importance, owing to their many uses and diverse properties. Among the newer polymers are the polyphosphazenes and polyphosphine oxides which are unique because of their high phosphorus content and chemical resistance. The chemical and physical properties of these polymers preclude the use of ordinary methods of elemental analysis. This is especially true in the initial step of decomposition and dissolution. However, accurate analysis can be accomplished by using the techniques described in this paper.

In the past, phosphorus has generally been determined in organic compounds by decomposing the sample, converting the phosphorus into orthophosphate, and measuring the orthophosphate in one of several ways. Decomposition of the organic material has been done by an acid digestion with nitric and perchloric acids,[1] nitric and sulphuric acids,[2-4] fuming nitric acid[5] and a mixture of nitric, sulphuric and perchloric acids.[6] None of these acid mixtures was adequate when used on phosphazenes

---

* This work was supported by the United States Atomic Energy Commission.

sample weighed and counted in this form. The method was checked by analysing commercial zirconyl chloride and standard rock samples for zirconium and hafnium by neutron-activation analysis.

Zusammenfassung—Radiozirkonium und Radiohafnium kann von allen anderen Radionukliden ausser Scandium und Protaktinium durch Niederschlag mit Mandelsäure aus 5–10*M* Salzsäure mittels handelsüblichem Zirkoniumchlorid als Träger getrennt werden. Scandium und Protaktinium werden durch Auflösen des Niederschlags in Natriumkarbonat und dann Zufügung von Bariumnitrat zum Niederschlagen von Bariumkarbonat entfernt, welch letzteres als Spülmittel fungiert. Zirkoniummandelat wird schliesslich wieder niedergeschlagen, und das Muster wird gewogen und in dieser Form berechnet. Das Verfahren wurde durch Analysieren von gewerblichem Zirkoniumchlorid und normalen Gesteinmustern von Zirkonium und Hafnium mittels Neutronaktivierungsanalyse geprüft.

Résumé—On peut séparer le radiozirconium et le radiohafnium de tous les autres radionuclides à l'exception du scandium et du protactinium par précipitation avec l'acide mandélique à partir d'acide chlorhydrique 5–10*M*, en utilisant le chlorure de zirconyle commercial comme entraîneur. On élimine le scandium et le protactinium en dissolvant le précipité dans du carbonate de sodium, puis en ajoutant du nitrate de baryum pour précipiter le carbonate de baryum qui agit comme un fixateur. Le mandélate de zirconium est finalement reprécipité et l'échantillon est pesé et compté sous cette forme. On a contrôlé la méthode en analysant le chlorure de zirconyle commercial et des échantillons de roche étalon pour le zirconium et le hafnium par analyse par activation de neutrons.

REFERENCES

1. W. S. Lyon, *Guide to Activation Analysis*, Van Nostrand, Princeton, 1964.
2. R. C. Koch, *Activation Analysis Handbook*, Academic Press, New York, 1960.
3. E. P. Steinberg, *The Radiochemistry of Zirconium and Hafnium*, National Nuclear Energy Series, NAS-NS 3011, Office of Technical Services, Washington, D.C. 1960.
4. C. K. Brooks, *Radiochimica Acta*, 1968, **8**, 167
5. C. A. Kumins, *Anal. Chem.*, 1947, **19**, 376.
6. R. B. Hahn, *ibid.*, 1951, **23**, 1259.
7. R. B. Hahn and L. Weber, *J. Am. Chem. Soc.*, 1955, **77**, 4777.
8. R. B. Hahn and E. S. Baginski, *Anal. Chim. Acta*, 1956, **14**, 45.

Talanta 1972. Vol. 19, pp. 1457 to 1460. Pergamon Press. Printed in Northern Ireland

Determination of phosphorus in phosphazenes and phosphines*

(*Received* 24 *April* 1972. *Accepted* 1 *May* 1972)

In recent years organic polymers have grown in importance, owing to their many uses and diverse properties. Among the newer polymers are the polyphosphazenes and polyphosphine oxides which are unique because of their high phosphorus content and chemical resistance. The chemical and physical properties of these polymers preclude the use of ordinary methods of elemental analysis. This is especially true in the initial step of decomposition and dissolution. However, accurate analysis can be accomplished by using the techniques described in this paper.

In the past, phosphorus has generally been determined in organic compounds by decomposing the sample, converting the phosphorus into orthophosphate, and measuring the orthophosphate in one of several ways. Decomposition of the organic material has been done by an acid digestion with nitric and perchloric acids,[1] nitric and sulphuric acids,[2-4] fuming nitric acid[5] and a mixture of nitric, sulphuric and perchloric acids.[6] None of these acid mixtures was adequate when used on phosphazenes

---

* This work was supported by the United States Atomic Energy Commission.

and phoshines. The method of Boos and Conn,[7] consisting of a sodium carbonate fusion, did not give a complete recovery of phosphorus. The same result was obtained when sodium peroxide was used in a Parr bomb as described by Burton and Riley.[8] Oxidation in an oxygen flask (Schöniger technique) has been used by several,[9-12] but the method did not work on these polymer samples. Very poor combustion was obtained, even on very small samples.

Measurements of the orthophosphate resulting from the decomposition of a sample has been done in several ways. The classical Lorenz[13] procedure based on the precipitation of phosphorus as ammonium phosphomolybdate has been used extensively. A drawback of this method is that an empirical factor is used in calculating the weight of phosphorus in the amount of precipitate collected; therefore, carefully defined conditions for precipitation must be followed. A colorimetric method based on the reduction of phosphomolybdic acid to molybdenum blue has been described.[14] Quinoline has also been used as a precipitating agent.[15,16] Precipitation of the orthophosphate as magnesium ammonium phosphate[17] provided the best results in this investigation.

EXPERIMENTAL

Procedure

Place a sample containing about 10 mg of phosphorus in a 10-ml Kjeldahl flask. Add 1 ml of conc. sulphuric acid and 0·5 ml of red fuming nitric acid, and heat gently with a micro-burner until foaming ceases. Increase the heat and boil the solution until it turns black. Continue adding fuming nitric acid, a few drops at a time, and heating until all of the black colour is gone and an amber solution remains. Heating must be strong enough to break down the organic material, but not severe enough to produce sulphur trioxide fumes. Add 4 drops of perchloric acid and heat the flask until the green colour is gone—but no longer. As the flask cools, acid condensed in the neck will drain into the solution and a colour, either green or brown, may reappear but will do no harm.

When the contents of the flask are cool, transfer them into a beaker, add 4 ml of concentrated nitric acid, and carefully dilute the solution to 80 ml with distilled water. Cover the beaker with a watch-glass and heat gently for 1 hr on a hot-plate. Neutralize the solution by adding ammonia solution. While the sample is still warm, add 10 ml of freshly filtered magnesia solution (55 g of magnesium chloride hexahydrate, 140 g of ammonium chloride, 350 ml of conc. ammonia solution, diluted with water to 1 litre) with stirring. After precipitation has started, add 20 ml of conc. ammonia solution. Allow to age for a minimum of 2 hr, filter off on an ignited and weighed 1A2 Berlin crucible, and wash with 100 ml of 20% v/v ammonia solution. Dry the precipitate at 105° for 1 hr, ignite in a muffle at 1000° for 1 hr, cool, and weigh. The gravimetric factor is 0·2783.

DISCUSSION

Since no standard polymers containing phosphorus were available, compounds of known composition and with similar phosphorus linkage were substituted. Triphenylphosphine was used extensively.

Decomposition of the sample and conversion of the phosphorus into orthophosphate was the most difficult part of the analysis. Of the many decomposition procedures tried, acid digestion was the only one which appeared promising. Refluxing in perchloric acid for 24 hr did not give quantitative recovery of phosphorus. Fuming nitric acid used alone did not completely decompose the samples. A mixture of sulphuric, nitric and perchloric acids was tried on triphenylphosphine, but results were about 5% (relative) low. The ignited $Mg_2P_2O_7$ obtained was often discoloured. Higher digestion temperatures were tried but resulted in losses by volatilization.

Substitution of red fuming nitric acid for conc. nitric acid gave good results; however, the amount of acid and the sequence of addition became significant. Most published methods require a small sample size, but a larger amount of polymeric material provided both a more representative sample and better accuracy. A sample size large enough to provide 30 mg of $Mg_2P_2O_7$ gave sufficient accuracy and was representative of the material tested. About 100 mg of triphenylphosphine were used and the amount of sulphuric acid varied from 0·5 to 5·0 ml. Best results were obtained with 1 ml; decomposition was difficult with more, and phosphorus was lost with less.

The addition of red fuming nitric acid was made as soon as the sample was mixed with the sulphuric acid: 0·5 ml worked best for the initial digestion; more than that slowed the reaction. When the straw colour was reached, the perchloric acid was added and the sample heated until the greenish colour disappeared. Earlier addition of perchloric acid causes foaming and does not accelerate the reaction. With this digestion technique, complete decomposition was always obtained regardless of sample composition. Also, the ignited product was always snow-white.

Precipitation with magnesia solution was slower when done hot, but a more easily filterable precipitate was obtained. The precipitate was aged for a minimum of 2 but not more than 24 hr, since the glass container was apparently attacked on prolonged aging and high results were obtained. Filtration was conveniently done with 1A2 Berlin crucibles.

Results

BDH standard triphenylphosphine was used to evaluate the procedure. Results obtained from eight determinations are shown in Table I.

TABLE I.—ANALYSIS OF TRIPHENYLPHOSPHINE (BDH).

Run	Phosphorus, %
1	11·71
2	11·86
3	11·77
4	11·97
5	11·88
6	11·94
7	11·91
8	11·86
Average	11·86 ± 0·09%

The average value of 11·86% compares well with the theoretical value of 11·81% for triphenylphosphine, thereby establishing the accuracy of the method. Precision, as shown by a standard deviation of 0·09%, was acceptable. Several Eastman chemicals similar to phosphines and phosphazenes were analysed by this procedure and the results shown in Table II illustrate the precision and accuracy of the method.

TABLE II.—P CONTENT OF VARIOUS EASTMAN CHEMICALS.

Compound	% P (theory)	% P (found)	No. of runs	Std. devn. % P
Carbomethoxymethylene-triphenylphosphorane	9·26	9·42	7	±0·06
Tri-*m*-tolyphosphine	10·18	10·14	4	±0·07
Benzyltriphenylphosphonium chloride	7·96	8·02	4	±0·08
Triphenylphosphine oxide	11·13	11·27	4	±0·10

A polyphosphazene, synthesized by J. Holovka, Sandia Laboratories, was analysed by the procedure and the results are shown in Table III. The precision, as shown in Table III, was excellent.

TABLE III.—PHOSPHORUS CONTENT OF PHOSPHAZENE POLYMER.

Run	P, %
1	26·76
2	27·10
3	26·96
4	26·95
Average	26·94 ± 0·14

Although no direct test for accuracy could be made in this case, it could be shown indirectly. A phosphazene has one nitrogen atom bound to each phosphorus atom; therefore an estimation of the accuracy of the phosphorus method can be based on analysis of the polymer for nitrogen. Nitrogen values obtained by the Kjeldahl technique yielded 12·1 ± 0·1%.[18] The 1:1 correspondence of nitrogen to phosphorus demands that the phosphorus content be 26·8 ± 0·2%. Comparison of this value with the 26·94 ± 0·14% phosphorus shown in Table III provides a strong argument for the accuracy of the method.

Acknowledgements—The author wishes to thank F. J. Conrad for his assistance and Dr. B. T. Kenna and J. C. Russell for their comments and suggestions during the course of this investigation.

Sandia Laboratories
Albuquerque, New Mexico 87115, *U.S.A.*
Sanford L. Erickson

Summary—An improved technique for the determination of phosphorus in organic phosphazenes and phosphines is described. An acid digestion using a mixture of fuming nitric, sulphuric and perchloric acids converts the organically bound phosphorus into orthophosphate. The orthophosphate is precipitated as magnesium ammonium phosphate, which is ignited to magnesium pyrophosphate. With this technique phosphorus was determined in several compounds. The results establish both good accuracy and precision for the method.

Zusammenfassung—Es wird ein verbessertes Verfahren zur Bestimmung von Phosphor in organischen Phosphazenen und Phosphinen beschrieben. Eine Säuredigestion mittels einer Mischung von rauchenden Stickstoff, Schwefelund Perchlorsäuren verwandelt den organisch gebundenen Phosphor in Orthophosphat. Das Orthophosphat wird als Magnesium–Ammonium–Phosphat niedergeschlagen, was zur Verbrennung in Magnesiumpyrophosphat erhitzt wird. Mit diesem Verfahren wurde Phosphor in mehreren Verbindungen bestimmt. Die Ergebnisse bezeugen günstige Genauigkeit und Präzision mit diesem Verfahren.

Résumé—On décrit une technique améliorée pour le dosage du phosphore dans les phosphazènes et phosphines organiques. Une digestion acide utilisant un mélange d'acides nitrique fumant, sulfurique et perchlorique convertit le phosphore lié organiquement en orthophosphate. L'orthophosphate est précipité à l'état de phosphate ammoniaco-magnésien, qui est calciné en pyrophosphate d'ammonium. Avec cette technique, on a dosé le phosphore dans plusieurs composés. Ces résultats établissent tant la bonne précision que la bonne fidélité de la méthode.

REFERENCES

1. A. R. Wreath, *J. Assoc. Offic. Agr. Chemists*, 1948, **31**, 800.
2. T. S. Ma and J. D. McKinley, Jr., *Mickrochim. Acta*, 1953, 4.
3. A. Steyermark, *Quantitative Organic Microanalysis*, pp. 192–7. Blakiston, Philadelphia, 1951.
4. R. A. Chalmers and D. A. Thomson, *Anal. Chim. Acta*, 1958, **18**, 575.
5. H. Medzihradszky-Schweiger and S. Kutassy, *Acta Chim. Acad. Sci. Hung.*, 1964, **41**, 265.
6. D. S. Kirkpatrick and S. H. Bishop, *Anal. Chem.*, 1971, **43**, 1707.
7. R. N. Boos and J. B. Conn, *ibid.*, 1951, **23**, 674.
8. J. D. Burton and J. P. Riley, *Analyst*, 1955, **80**, 391.
9. K. D. Fleischer, B. C. Southworth, J. H. Hodecker and M. M. Tuckerman, *Anal. Chem.*, 1958, **30**, 152.
10. L. E. Cohen and F. W. Czech, *Chemist-Analyst*, 1958, **47**, 86.
11. R. Belcher and A. M. G. McDonald, *Talanta*, 1958, **1**, 185.
12. B. C. Stanley, S. H. Vannier, L. D. Freedman and G. O. Doak, *Anal. Chem.*, 1955, **27**, 474.
13. N. Z. Lorenz, *Z. Anal. Chem.*, 1912, **51**, 161.
14. G. Ingram, *Methods of Organic Elemental Microanalysis*, pp. 339–348. Reinhold, New York, 1962.
15. H. N. Wilson, *Analyst*, 1951, **76**, 65.
16. T. R. F. W. Fennell and J. R. Webb, *Talanta*, 1959, **2**, 105.
17. R. S. Young, *Industrial Inorganic Analysis*, p. 221. Chapman & Hall, London, 1953.
18. R. M. Merrill, personal communication, 1971.

Talanta, 1972, Vol. 19, pp. 1461 to 1465. Pergamon Press. Printed in Northern Ireland

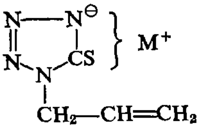
New tests for the detection of azide

(*Received* 10 *January* 1972. *Accepted* 17 *February* 1972)

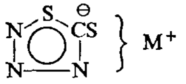
FEW TESTS are available for the analysis and identification of azides.[1-7] The classical Werner test,[1] modified by Sommer and Pincus,[2] and by Feigl[3] is based on the complete destruction of nitrate by azide in the presence of dilute acid ($HN_3 + HNO_2 \rightarrow H_2O + N_2O + N_2$); the reaction, however, invariably requires a blank test. The ferric chloride test[4] for azides, giving the red colour of soluble ferric azide, $Fe(N_3)_3$, is subject to interference by thiocyanate. The detection of azide ion by precipitation with nitron, followed by infrared spectroscopy on the precipitate[5] is only possible for high azide concentrations and even then has not always been found feasible. The test for azide with silver chromate-impregnated paper[6] lacks rapidity and suffers from interferences. The uranyl nitrate–ascorbic acid test for nitrite[7] is also useful, but to a limited extent, for the detection of azide and its differentiation from nitrite.

The present communication describes two simple, rapid, and reliable colour tests for the detection of azide; neither is subject to interference by thiocyanate. The first is based on the interaction of azide with allyl isothiocyanate in aqueous medium, forming a novel heterocyclic compound 1-allyl-2-tetrazoline-5-thione (I), which forms a deep yellow precipitate with bismuth. Addition of pyridine enhances the colour intensity, or turns the precipitate yellowish-orange. This test can be done in a test-tube, on a spot-plate, or on filter paper. A modification of the test starts with allylamine, which is converted into allyl isothiocyanate by treatment with carbon disulphide and hydrogen peroxide in presence of a little diethylamine.[8]

The second test is based on the reaction of azide with carbon disulphide in aqueous acetone to form 1,2,3,4-thiatriazoline-5-thionate (II); the latter gives a yellow precipitate with copper(II) or bismuth. The colour intensity of the copper precipitate is slightly increased on addition of pyridine; the bismuth precipitate turns yellowish-orange or deep orange on treatment with pyridine.



I



(M = a univalent cation, *e.g.*, Na^+, K^+, NH_4^+)

II

Both tests are highly specific for azide, as no other anion gives these tests. Milligram quantities of azide can be detected by these tests. The tests are, however, applicable only to water-soluble azides; heavy metal azides which are practically insoluble in water fail to give a positive response.

EXPERIMENTAL

Reagents

Hydrogen peroxide, 20-vol.
Bismuth nitrate solution, 1% w/v in dilute nitric acid.
Copper sulphate solution, 0·5% w/v.

Procedures

Allyl isothiocyanate test. Take 3 ml of water in a test-tube, add 2 drops of allyl isothiocyanate and ~20 mg of test solid or 1 ml of aqueous test solution (the azide content in either test material should be 5–10 mg). Heat the tube in boiling water for 2–3 min. A clear colourless solution is obtained. Remove the tube and proceed in any of the following ways.

(*a*) To 1 ml of bismuth nitrate solution in a separate test-tube, add ~0·5 ml of the test solution. Azide is indicated by formation of a fine canary yellow precipitate. On addition of 1 or 2 drops of pyridine the precipitate turns very deep yellow, and becomes coarser and may adhere to the walls of the tube. Sometimes a transient precipitate is obtained but becomes permanent on addition of more test solution.

(*b*) Place a drop of bismuth nitrate solution in a depression on a spot-plate and add two drops of test solution. If azide is present, a canary yellow precipitate appears.

(*c*) Place a drop of bismuth nitrate solution on a filter paper, and add one drop of the test solution. A yellow spot indicates azide.

Allylamine test via the formation of allyl isothiocyanate. Take 3 drops of allylamine, 2 drops of carbon disulphide, and 1 drop of diethylamine in a test-tube, and carefully add 4 or 5 drops of 20-vol hydrogen peroxide. A brisk exothermic reaction ensues which soon subsides. This reaction forms allyl isothiocyanate, which has the sharp characterictic smell of mustard oil. Add a little of the solid or aqueous test sample (containing 5–10 mg of azide) and 2 ml of water, and then proceed further as described above. (In this test, the sample may be added even at the start.)

Carbon disulphide test. Take 3 ml of water in a test-tube, add 3 drops of carbon disulphide, ~20 mg of test solid and 1·5 ml of acetone. Heat the tube in boiling water for 1–2 min until a clear colourless solution is obtained. Prolonged heating must be avoided. Remove the tube and proceed in any of the following ways.

(*a*) To 1 ml of copper sulphate solution in a separate tube, add several drops of the test solution. A yellow precipitate which turns fairly deep yellow on addition of a drop of pyridine indicates azide.

(*b*) To 1 ml of bismuth nitrate solution add 0·5–1·0 ml of test solution. A yellow precipitate which turns yellowish-orange or deep orange on addition of 1 or 2 drops of pyridine indicates azide.

(*c*) Place a drop of bismuth nitrate solution on a filter paper and add a drop of test solution. A deep yellow spot indicates azide.

RESULTS AND DISCUSSION

Effect of pH

Both the allyl isothiocyanate and carbon disulphide tests are to be conducted at pH $\geqslant 7{\cdot}0$. At lower pH, the azide is likely to be decomposed and completely expelled (even at fairly low temperature, *ca.* 37°) in the form of hydrazoic acid, HN_3.

Interferences

None of the tests described suffers from interference by Cl^-, Br^-, I^-, F^-, SO_3^{2-}, SO_4^{2-}, NO_3^-, PO_4^{3-}, CN^-, and SCN^- ions. Nitrite does cause some interference in the carbon disulphide test, but only when present in larger amounts. Sulphides cause serious interference as the product is masked by the simultaneous formation of black copper sulphide in the carbon disulphide test and black bismuth sulphide in both the allyl isothiocyanate and carbon disulphide tests. This interference can be avoided by preliminary oxidation of the neutral or alkaline test solution with several drops of hydrogen peroxide.[8] Hydrogen peroxide treatment also removes thiosulphates.

Negative results

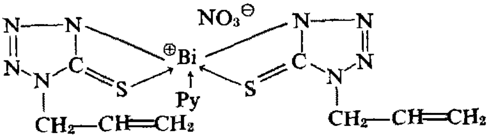
Heavy metal azides, being practically insoluble in water, yield a negligible quantity of azide ions in solution, and so fail to give any of the tests reported here.

Nature of the product in the allyl isothiocyanate test

The interaction of azide with organic isothiocyanates in solution is known to give 1-substituted 2-tetrazoline-5-thiones.[9–13] Generally a heating period of 4–8 hr is required for complete reaction. The reaction rate of a large number of isothiocyanates (aromatic and aliphatic) with azide has been studied, but only with allyl isothiocyanate is the reaction rapid. For qualitative purposes the reaction goes sufficiently within 2 min, giving 1-allyl-2-tetrazoline-5-thione (I). This compound has been described earlier[11,14] as 1-allyl-5-mercaptotetrazole.

A quantitative study of a different tetrazolinethione compound (1-phenyl-2-tetrazoline-5-thione) with bismuth has been reported by Stevancevic.[15–17] We have studied the reaction of a number of 1-substituted 2-tetrazoline-5-thiones with bismuth,[18] and established that an internal bismuth complex is formed in all cases. The complex is invariably yellow. The allyl isothiocyanate test for azide is based on these facts. We have found that when reacted with a solution of bismuth nitrate 1-allyl-2-tetrazoline-5-thione gives a complex having the formula $Bi(L)_2NO_3$, which on treatment with pyridine gives $Bi(L)_2NO_3.Py$. The metal and sulphur analysis confirms a 1:2 (metal:ligand) ratio in these complexes. Found: Bi, 37·2%, S, 11·8%; required for $Bi(C_8H_{10}N_9O_3S_2)$: Bi, 37·7%, S, 11·5%. Found: Bi, 32·4%, S, 10·7%; required for $Bi(C_{13}H_{15}N_{10}O_3S_2)$ or $Bi(L)_2NO_3.Py$: Bi 33·0%, S, 10·1%.

A study of the infrared absorption spectra (Perkin-Elmer Model 521, KBr discs) of the yellow complexes of bismuth, made on the pattern reported earlier,[19–26] showed that the metal ion is co-ordinated through both the thiocarbonyl sulphur atom and a nitrogen atom of the ligand. In consistence with these findings, III is proposed as the most probable structure for the bismuth 1-allyl-2-tetrazoline-5-thione complex pyridine adduct, *i.e.*, bis(1-allyl-2-tetrazoline-5-thionato)pyridinonitratobismuth(III).



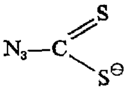
III

Nature of the product in the carbon disulphide test

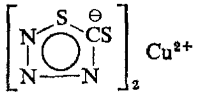
Sommer[27] was the first to observe that the interaction of azide with carbon disulphide results in the formation of azidodithiocarbonate ions (IV). This view was accepted by some other workers,[28,29] but later Lieber *et al.*[30–32] rejected the previous view, and confirmed that the product is undoubtedly 1,2,3,4-thiatriazoline-5-thionate(II). Our findings on the elemental and infrared spectroscopic analysis of pure 1,2,3,4-thiatriazoline-5-thione, prepared by the method described in the literature,[32] confirm this view. The negative charge on the thiatriazolinethionate ions is considered to be delocalized over the entire heterocyclic ring.[32]

The yellow product obtained in the carbon disulphide test has been found to be a co-ordination complex of copper(II) with 1,2,3,4-thiatriazoline-5-thionate. The elemental analysis confirms a 1:2 (metal:ligand) ratio. Found: C, 7·9%, H, 0·0%, S, 42·3%, Cu, 20·8%; required for $Cu(C_2N_6S_4)$: C, 8·0%, H, 0·0%, S, 42·6%, Cu, 21·1%. The infrared absorption bands of the copper complex nearly matched those reported by Beck and Fehlhammer[33] for the palladium(II) complex of 1,2,3,4-thiatriazoline-5-thione (triphenylphosphine adduct).

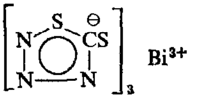
From these findings, V is proposed as the likely structure for the copper complex, *i.e.*, bis(1,2,3,4-thiatriazoline-5-thionate)copper(II). This substance slowly decomposes on storage.



IV



V



VI

It was not possible to analyse the yellow product obtained by the action of bismuth nitrate solution on 1,2,3,4-thiatriazoline-5-thionate formed in the carbon disulphide test, because the product always underwent decomposition with dangerous detonation, during attempts to dry it. However, it seems probable that it will be the bismuth analogue of the copper complex just described, and VI is tentatively proposed as its formula.

Department of Chemistry
V.S.S.D. College
Kanpur-2, India

G. S. JOHAR

Summary—Two new, simple, reliable, and specific colour tests are described for the detection of azide. In one, the azide is heated with allyl isothiocyanate and water to form 1-allyl-2-tetrazoline-5-thione in solution; the latter gives a yellow precipitate on treatment with bismuth nitrate solution. Pyridine enhances the intensity of the colour. The allyl isothiocyanate can be produced *in situ* by treating allylamine with carbon disulphide, diethylamine and hydrogen peroxide. In the other test the azide is heated with carbon disulphide, water and acetone, resulting in the formation of 1,2,3,4-thiatriazoline-5-thione which gives a yellow precipitate with Cu(II) or Bi(III). Pyridine again enhances the colour. The method is applicable to 5–10 mg of soluble azides, but insoluble azides cannot be tested. CN^-, SCN^-, and other common anions do not interfere. Only S^{2-} interferes by masking the colour (black CuS or Bi_2S_3 is precipitated). NO_2^- in larger amounts interferes in the second test.

Zusammenfassung—Es werden zwei neue, einfache, zuverlässige und bestimmte Farbenteste zur Feststellung von Azid beschrieben. In einem wird das Azid mit Allyl-Isothiocyanat und Wasser erhitzt, um 1-Allyl-2-Tetrazolin-5-Thion in Lösung zu bilden. Letzteres gibt bei Behandlung mit Wismuthnitratlösung einen gelben Niederschlag. Pyridin verstärkt die Intensität der Farbe. Das Allyl Isothiocyanat kann in ursprünglicher Lage durch Behandlung des Allylamins mit Karbonbisulfid, Diäthylamin und Wasserstoffsuperoxyd produziert werden. In dem anderen Test wird das Azid mit Karbonbisulfid, Wasser und Aceton erhitzt, wodurch sich 1,2,3,4-Thiatriazolin-5-Thion bildet, was einen gelben Niederschlag mit Cu(II) oder Bi(III) gibt. Wieder verstärkt Pyridin die Farbe. Das Verfahren kann bis zu 5–10 mg löslicher Azide verwandt werden, unlösliche Azide können jedoch nicht geprüft werden. CN^-, SCN^- und andere übliche Anionen haben keinen störenden Einfluss. Nur S^{2-} hat durch Tarnung der Farbe (schwarzes CuS oder Bi_2S_3 wird niedergeschlagen) störenden Einfluss. NO_2^- hat in grösseren Mengen einen störenden Einfluss in dem zweiten Test.

Résumé—On décrit deux nouveaux essais colorés simples, sûrs et spécifiques pour la détection de l'azide. Dans l'un, l'azide est chauffé avec l'isothiocyanate d'allyle et l'eau pour former la 1-allyl 2-tétrazoline 5-thione en solution; cette dernière donne un précipité jaune par traitement avec une solution de nitrate de bismuth. La pyridine exalte l'intensité de la coloration. L'isothiocyanate d'allyle peut être produit *in situ* en traitant l'allylamine par le sulfure de carbone, la diéthylamine et l'eau oxygénée. Dans l'autre essai, l'azide est chauffé avec du sulfure de carbone, de l'eau et de l'acétone, avec pour conséquence la formation de 1,2,3,4-thiatriazoline 5-thione qui donne un précipité jaune avec Cu(II) ou Bi(III). La pyridine exalte de nouveau la coloration. La méthode est applicable à 5–10 mg d'azides solubles, mais les azides insolubles ne peuvent être essayés. CN^-, SCN^- et autres anions communs ne gênent pas. Seul S^{2-} gêne en dissimulant la coloration (il précipite CuS ou Bi_2S_3 noirs). NO_2^- en quantités plus importantes gêne dans le second essai.

REFERENCES

1. E. A. Werner, *Proc. Chem. Soc.* 1913, **28,** 257.
2. F. Sommer and H. Pincus, *Ber.*, 1915, **48,** 1963.
3. F. Feigl, *Spot Tests in Inorganic Analysis*, 5th Ed., p. 287. Elsevier, Amsterdam, 1958.
4. F. Feigl, *Rec. Trav. Chim.*, 1939, **58,** 476.
5. R. J. Magee, S. A. F. Shahine and C. L. Wilson, *Mikrochim. Acta*, 1964, 479.
6. J. G. Sabo, *Chemist-Analyst*, 1965, **54,** 110.
7. G. S. Johar and U. Agarwala, *Sci. Cult., Calcutta*, 1970, **36,** 521.
8. G. S. Johar, U. Agarwala and P. B. Rao, *Indian J. Chem.*, 1970, **8,** 759.
9. V. E. Oliveri-Mandala and F. Noto, *Gazz. Chim. Ital.*, 1913, **43,** 304.
10. *Idem, ibid.*, 1914, **44,** 670.
11. E. Lieber and J. Ramachandran, *Can. J. Chem.*, 1959, **37,** 101.
12. E. Lieber and R. Slutkin, *J. Org. Chem.*, 1962, **27,** 2214.
13. G. S. Johar and U. Agarwala, *Sci. Cult., Calcutta*, 1969, **35,** 479.
14. R. Stolle and A. Strittmatter, *J. Prakt. Chem.*, 1932, **133,** 60.
15. D. B. Stevancevic and V. G. Antonijevic, *Bull. Inst. Nucl. Sci. "Boris Kidrich", Belgrade*, 1961, **12,** 109.
16. D. B. Stevancevic, *ibid.*, 1962, **13,** 47.
17. *Idem, ibid.*, 1963, **14,** 67.
18. G. S. Johar and U. Agarwala, *Curr. Sci. (India)*, 1969, **38,** 492.
19. U. Agarwala, V. A. Narayan and S. K. Dikshit, *Can. J. Chem.*, 1967, **12,** 1061.
20. U. Agarwala and S. K. Dikshit, *J. Inorg. Nucl. Chem.*, 1968, **30,** 1245.
21. U. Agarwala and B. Singh, *ibid.*, 1969, **31,** 2515.
22. U. Agarwala, *Proc. Chem. Symp. 1st*, 23–26 Sept., 1969 (Publ. 1970), **1,** 160; *Chem. Abstr.*, 1971, **74,** 18884*d*.

23. U. Agarwala and B. Singh, *Indian J. Chem.*, 1969, **7**, 726.
24. G. S. Johar and U. Agarwala, *J. Indian Chem. Soc.*, 1970, **47**, 904.
25. *Idem*, *Talanta*, 1970, **17**, 355.
26. G. S. Johar, *LABDEV*, *Kanpur*, *India*, 1970, **8A**, 114.
27. F. Sommer, *Ber.*, 1915, **48**, 1833.
28. L. F. Audrieth, *Chem. Rev.*, 1934, **15**, 169.
29. N. Hofman-Bang and B. Holten, *Acta Chem. Scand.*, 1951, **5**, 333.
30. E. Lieber, J. Ramachandran, C. N. R. Rao and C. N. Pillai, *Can. J. Chem.*, 1959, **37**, 563.
31. E. Lieber, C. N. Pillai, J. Ramachandran and R. D. Hites, *J. Org. Chem.*, 1957, **22**, 1750.
32. E. Lieber, E. Oftedahl and C. N. R. Rao, *ibid.*, 1963, **28**, 194.
33. W. Beck and W. P. Fehlhammer, *Angew. Chem. Intern. Ed. Engl.*, 1967, **6**, 169.

Talanta, 1972, Vol. 19, pp. 1465 to 1467. Pergamon Press. Printed in Northern Ireland

Potentiometric titration of heterocyclic nitrogen bases in non-aqueous media

(*Received* 15 *February* 1972. *Accepted* 24 *May* 1972)

PERCHLORIC ACID has been widely used for potentiometric titration of heterocyclic nitrogen bases in acetic acid and other non-aqueous media, with various electrodes.[1-8] We have now examined the use of chlorosulphonic acid as titrant in methyl ethyl ketone–acetic acid medium, for the same purpose, in continuation of our work with this titrant.[9,10]

EXPERIMENTAL

Reagents

Methyl ethyl ketone.
Acetic acid. Purified by refluxing with acetic anhydride for 8 hr and then distilling.
Chlorosulphonic acid.
Quinoline. Dried over anhydrous magnesium sulphate and then distilled.
Isoquinoline. Distilled at reduced pressure.
Picolines. Purified by the method recommended by Vogel.[11]
2,6-*Lutidine.* Distilled.
Acridine.
Sodium acetate trihydrate.
The purity of the liquid bases was checked from precision density values and boiling points.

Procedures

Preparation of titrant. Approximately $1M$ chlorosulphonic acid in acetic acid was prepared by adding about 250 ml of acetic acid to about 7 ml of cooled chlorosulphonic acid. This solution was then diluted with methyl ethyl ketone to obtain a solution of the desired concentration, which was standardized by titration with sodium acetate in methyl ethyl ketone–acetic acid (1:1) medium either potentiometrically (glass and calomel electrodes) or with Methyl Orange indicator. Earlier work[9] had shown that up to 1% of water does not affect the potential change at the end point. The amount of hydrated sodium acetate used introduces only about 0·1% of water into the system, so there is no interference.

Preparation of base solutions. Solutions of the bases ($0{\cdot}5M$) in acetic acid were prepared. Aliquots of these were successively diluted with methyl ethyl ketone to yield a series of concentrations.

Potentiometric titrations. Titrations of $0{\cdot}5M$ acridine with $0{\cdot}1M$ chlorosulphonic acid were done (glass and calomel electrodes) in a mixed solvent of methyl ethyl ketone and acetic acid in 1:1, 5:1, 10:1 and 20:1 v/v ratio. The slope of the potentiometric curves in the vicinity of the end-point increased with increase in the proportion of methyl ethyl ketone, but with high concentrations of the ketone the potential during the initial stages of titration did not conform to regular Nernstian behaviour. The 1:1 medium was therefore preferred. The glass electrode gave a steeper slope at the end-point (30 mV/0·1 ml) than the chloranil or quinhydrone electrodes (both 18 mV/0·1 ml).

RESULTS AND DISCUSSION

The end-point was determined by the calculation method.[12] The results are given in Table I, and show that semimicro quantities of heterocyclic nitrogen bases can be determined in this way with an

10. *Idem*, *Proc. Indian Acad. Sci.*, 1972, in the press.
11. A. I. Vogel, *Practical Organic Chemistry*, 3rd Ed., p. 177. Longmans, London, 1959.
12. I. Gyenes, *Titration in Non-Aqueous Media*, p. 186. Iliffe, London, 1967.
13. V. K. Kondratov, N. D. Rusyanova and N. V. Malysheva, *Zh. Analit. Khim.*, 1966, **21** (8), 996.

Talanta, 1972, Vol. 19, pp. 1467 to 1470. Pergamon Press. Printed in Northern Ireland

Rapid determination of selenium and tellurium by atomic-absorption spectrophotometry

(*Received* 13 *March* 1972. *Accepted* 7 *May* 1972)

FOR THE PAST few decades, the literature of applied geochemistry has described the possibility of volatile elements forming "halos" around precious and base-metal mineralization.[1] The elements commonly considered in this context are mercury, arsenic, selenium and tellurium and it is assumed that such "halo" or "pathfinding" elements would present an indirect but larger target for geochemical exploration using either soil or vegetation sampling techniques.

A suitable analytical method for these elements, except mercury, should allow for the determination of concentrations as low as 0·1 ppm and at a rate of at least fifty samples per day.

Because scattering problems are particularly serious at the short wavelengths of the most sensitive resonance lines of selenium and tellurium (*ca.* 200 nm), it is seldom possible to determine these elements directly by atomic-absorption spectrophotometry and therefore a separation step[2] is essential. Such a separation step should remove all possible interfering species, thereby allowing the use of the low-temperature nitrogen–hydrogen flame. This flame affords greater sensitivity for selenium and tellurium than the conventional air–acetylene flame.

A rapid method[3] has recently been developed for determining selenium in geological materials. This method involved co-precipitation of selenium with an arsenic carrier. Further work was carried out with a view to determining arsenic, selenium and tellurium in the same solution by a co-precipitation technique followed by atomic-absorption analysis of the redissolved precipitate. Although it was not possible to obtain quantitative recoveries of all three elements, good results were obtained for selenium and tellurium when arsenic was employed as a carrier. The method so developed is reported in this paper.

EXPERIMENTAL

Apparatus

The atomic-absorption measurements were done with a Techtron AA5 unit using the following conditions:

Source: standard ASL hollow cathode lamps
Lamp currents: Se—5 mA, Te—7 mA
Wavelengths: Se—196·0 nm, Te—214·2 nm
Slit width: 0·2 mm
Burner: standard 10-cm laminar burner
Photomultiplier: R106 (Hamamatsu TV. Co.)
Gas mixture: nitrogen, flow-rate 7·5 scale units (15 psig)
hydrogen, flow-rate 3·5 scale units (2 psig)
Scale expansion: up to ×8. Damping was not used.

Reagents

Analytical grade perchloric acid (60%).

Analytical grade nitric acid (s.g 1·42).

Hydrochloric acid, 6M.

Hypophosphorous acid, 30% w/v aqueous solution.

Arsenic solution. Dissolve 250 mg of arsenic trioxide and 2 g of sodium hydroxide in water and dilute to 200 ml.

Standard selenium solution. Dissolve 50 mg of selenium in hot conc. nitric acid and dilute to 500 ml with water (100 ppm Se).

Standard tellurium solution. Dissolve 0.0625 g of tellurium dioxide with 2 g of sodium hydroxide in about 100 ml of water and make up to 500 ml (100 ppm Te).

Digestion of geological samples

One-g samples of soil, rock, gossan or sulphide ore were digested with 15 ml of a 1:1 mixture of nitric and hydrofluoric acids in polypropylene beakers, at 80° over a water-bath, and then evaporated to dryness (in about 4 hr).

Digestion of biological samples

One-g samples of dried vegetation (leaves, twigs, bark or wood) were digested with 10 ml of a 4:1 mixture of nitric and perchloric acids in test-tubes (20 × 150 mm). These tubes were placed in close-fitting recesses in a thermostatically-controlled aluminium heating block. One glass bead and one drop of kerosene were added to each tube and digestion was begun at 70°. After 8 hr, the temperature was increased to 130°, whereby all the nitric acid was boiled off overnight. The solutions were then allowed to cool. The bead and kerosene were used to prevent bumping and frothing of the digestion mixture.

Separation of selenium and tellurium

The residues were leached with 20 ml of hot 6*M* hydrochloric acid for 15 min and the mixtures were then transferred to 50-ml centrifuge tubes. The solutions were centrifuged for 3 min, and decanted into clean test-tubes, thus discarding the siliceous residues. Two ml of arsenic solution were added to each tube, and after mixing, were followed by 8 ml of 30% hypophosphorous acid. The tubes were placed for 15 min in a hot water-bath (80°) and were then allowed to cool and stand for at least 8 hr to allow complete flocculation of the brown-black arsenic precipitate.

The next stage of the procedure was complete removal of the supernatant liquid by means of suction through a glass tube drawn out to a capillary. The precipitate was washed with 10 ml of 6*M* hydrochloric acid, centrifuged, and the supernatant phase removed as before. This residue was dissolved in 2 ml of 1·6*M* nitric acid, which was most easily accomplished by adding 0·2 ml of conc. (16*M*) nitric acid to dissolve the precipitate, then adding 1·8 ml of water. For larger quantities of selenium and tellurium (>100 μg) 20 ml of 1·6*M* acid are added to ensure complete dissolution.

Atomic-absorption determination of selenium and tellurium

For routine samples, standards comprised 1·5 and 10 ppm selenium and tellurium in 1·6*M* nitric acid. For higher concentrations of these elements, standards containing 10, 20, 40, 60 and 100 ppm were used. Beer's law was obeyed up to 10 ppm. Under the routine instrumental conditions, sensitivity for both selenium and tellurium is better than 0·7 ppm.

RESULTS AND DISCUSSION

Digestion of plant material

It is certain that significant losses of selenium, at least, would occur on dry-ashing vegetation. Hence wet-ashing with a nitric-perchloric acid mixture is essential for determination of total selenium and/or tellurium concentrations.

During the digestion stage for plant material, 10 ml of a 4:1 nitric-perchloric acid mixture are adequate to digest most vegetation samples (12 ml of nitric acid may be necessary in some cases) provided the nitric acid is not boiled off too quickly, as charring and loss of volatile elements may then result. All nitric acid must be removed before the addition of the hypophosphorous acid in the reduction step and hence a two-stage digestion process is used, the second stage being at temperatures above the boiling point of nitric acid (121°) though lower than the temperature of the constant-boiling mixture of perchloric acid and water.

Recoveries of selenium and tellurium

Experiments were carried out to determine the relationship between the amount of arsenic added and the recovery of added selenium and tellurium. Recovery of added selenium and tellurium ranging from 1 to 100 μg was complete when 2 ml of arsenic solution (~1800 μg of As) were used for the separation procedure. However, recoveries were only about 75% when settling times shorter than 8 hr were used. Recovery tests were carried out by adding known amounts of both elements (0–200 μg) to a number of soil samples of known composition and with non-detectable amounts of selenium and tellurium. Full recovery of both elements was achieved even when iron was present in high concentrations.

Reproducibility and accuracy of the method

Table I summarizes analytical data for selenium and tellurium in a standard sulphide ore,[4] and for replicates of five other selected samples chosen for their variable range of selenium and tellurium concentrations. The results show that the reproducibility is more than adequate for geochemical prospecting. The agreement with values obtained by other workers using different methods indicates that the accuracy of this method is also satisfactory. The results appear to be the first for selenium and tellurium in the C.A.A.S. standard sulphide ore.

TABLE I.—RESULTS OF REPLICATE DETERMINATIONS OF SELENIUM AND TELLURIUM IN GEOLOGICAL AND PLANT SAMPLES.

Sample	No. of determinations	Selenium, ppm		Tellurium, ppm	
		Mean	Range	Mean	Range
Acacia leaves (Aust.)	4	130	121–146	< 0·1	–
Acacia twigs (Aust.)	4	34	32–38	< 0·1	–
Argentiferous quartz (N.Z.)	4	9·3	8·8–9·8	1850	1800–1950
Auriferous pyrite (Aust.)	3	5·6	5·5–5·7	2·5*	2·4–2·6
C.A.A.S. sulphide ore[4] (Canada)	12	20·6†	18–22	2·0*	1·9–2·1
Uranium ore (U.S.A.)	12	4700	4000–4900	< 0·1	–

* A colleague (Mr. K. Arundale) employed a distillation method[5] for the determination of tellurium, and obtained a mean of 1·8 ppm for the auriferous pyrite and 1·86 ppm for the C.A.A.S. sulphide ore.

† Dr J. H. Watkinson, Ruakura Research Centre, using his colorimetric method,[6] obtained an average of 23·8 ppm Se for the C.A.A.S. sulphide ore.

Limits of detection

If *limit of detection* is defined as a signal equal to twice the noise level, the method appears to have a detection limit of about 0·1 ppm for selenium and tellurium, with a conventional burner. This should be improved considerably by using the *flame-in-tube* method.[7]

Conclusions

It is concluded that the method has the required rapidity, reproducibility, and sensitivity for geochemical prospecting. For vegetation samples containing background selenium levels[8] (*i.e.*, 0·05 ppm on the dry weight), the *flame-in-tube* method would have to be used for the atomic-absorption part of this procedure.

Acknowledgements—We are most grateful to Mr. K. Arundale and Dr. J. H. Watkinson for providing collaborative tellurium and selenium results, and to Western Mining Corporation for financial support.

Department of Chemistry, Biochemistry & Biophysics
Massey University
Palmerston North
New Zealand

B. C. SEVERNE
R. R. BROOKS

Summary—A rapid method has been developed for the determination of selenium and tellurium in geological and biological samples. It involves acid digestion of the sample with mineral acids, addition of arsenic as a carrier, reduction of arsenic to co-precipitate selenium and tellurium, dissolution of the precipitate in dilute nitric acid and subsequent determination of selenium and tellurium by conventional atomic-absorption spectrophotometry. Selenium and tellurium have been measured on a routine basis, down to 0.1 ppm.

Zusammenfassung—Es ist eine Schnellmethode zur Bestimmung von Selen und Tellur aus geologischen und biologischen Mustern entwickelt worden. Sie umfasst Säuredigestion des Musters mit Mineralsäuren, Zusatz von Arsen als ein Träger, Reduktion von Arsen auf zusammen fällbares Selen und Tellur, Auflösung des Niederschlags in verdünnter Salpetersäure und darauffolgende Bestimmung von Selen und Tellur durch übliche atomische Absorptionspektralphotometrie. Selen und Tellur sind auf üblicher Grundlage bis auf 0,1 ppm hinunter gemessen worden.

Résumé—On a élaboré une méthode rapide pour le dosage du sélénium et du tellurium dans des échantillons géologiques et biologiques. Elle comprend la digestion acide de l'échantillon avec des acides minéraux, l'addition d'arsenic comme entraîneur, la réduction de l'arsenic pour coprécipiter le sélénium et le tellurium, la dissolution du précipité en acide nitrique dilué et la détermination subséquente du sélénium et du tellurium par spectrophotométrie d'absorption atomique classique. On a mesuré le sélénium et le tellurium de manière courante jusqu'à 0,1 p.p.m.

REFERENCES

1. H. V. Warren and R. E. Delavault, *Proc. Geochem. Expl Symp., 20th Int. Geol. Congress Mexico City*, 1959, 255.
2. H. M. Nakagawa and C. E. Thompson, *U.S. Geol. Surv. Prof. Paper*, 1968, No. 600-B, B 123.
3. B. C. Severne and R. R. Brooks, *Anal. Chim. Acta*, 1972, **58**, 216.
4. G. R. Webber, *Geochim. Cosmochim. Acta*, 1965, **29**, 229.
5. C. E. S. Davis, W. E. Ewers and A. B. Fletcher, *Proc. Australas. Inst. Min. Metall.*, 1969, No. 232, 67.
6. J. H. Watkinson, *Anal. Chem.* ,1966, **38**, 92.
7. J. E. Allan, *Proc. 4th Aust. Spectroscopy Conf., Canberra*, 1963.
8. M. R. Gardiner, J. Armstrong, H. Tels and R. N. Glencross, *Aust. J. Exptl. Ag. Anim. Husb.*, 1962, **2**, 261.

Talanta, 1972, Vol. 19, pp. 1470 to 1474. Pergamon Press. Printed in Northern Ireland

Developments in indicators

(*Received* 30 *September* 1971. *Revised* 11 *February* 1972. *Accepted* 18 *March* 1972)

IN RECENT years narrow-range pH indicators have been introduced.[1,2,3] In addition, a pH indicator changing through three distinct colours has been recommended.[4] α-Aminonaphthaleneazoantipyrine changes from a light colour to a dark one, and then to a light one again.[5] Complementary tristimulus colorimetry has been used for calculating the ratios of the individual components of mixed indicators, necessary for the formation of a transition colour.[6]

Very weak acids which cannot be titrated successfully with alkali in aqueous solution, may be titrated in basic non-aqueous solvents. This approach offers many new possibilities but is also not without some difficulties. Methods are known based on the principle that if the stability constant of a complex is too low, it may be possible to add some substance that will increase the conditional constant.[7] In this way boric acid, which is too weak to be titrated directly, can be transformed into a stronger acid by adding mannitol, and glycine can be titrated after addition of copper sulphate, with Methyl Red as indicator.

Metal–metallochromic indicator complexes can be employed as acid–base indicators, when the formation of a complex is accompanied by the release of more than one proton per indicator molecule. Such an indicator can provide a whole range of pH indicators by variation of the metal ion used.[8]

This paper describes the application of such indicator systems to the titration of weak acids. When an alkali is used as titrant, and a metal indicator together with a metal salt as the acid-base indicator, the colour change occurs at a definite pH, the acid form of the indicator turning not into the alkaline form but into a complex. Some of the possible applications of this principle are illustrated.

1-(2′,4′-Dinitrobenzene)-2-acetyl hydrazine (DBAH) forms green complex with Cu^{2+}, Cu^{+} and to a slight extent with Ni^{2+}. Copper forms a 1:1 complex in aqueous medium; the stability constant was determined spectrophotometrically at pH 8·5 as $\log \beta = 8{\cdot}5$ ($I = 0{\cdot}1$.) The complex is stable at pH 7·8–9·0.[9]

In a conventional acid–base indicator the transition interval is about 2 pH units. In the case of a metal–metallochromic indicator having iminodiacetic acid groups where n protons could be released at the same time, the pH interval for the complete colour change would be $2/n$.[8] In the copper–DBAH indicator system the colour change does not occur over a pH range because the complex

Résumé—On a élaboré une méthode rapide pour le dosage du sélénium et du tellurium dans des échantillons géologiques et biologiques. Elle comprend la digestion acide de l'échantillon avec des acides minéraux, l'addition d'arsenic comme entraîneur, la réduction de l'arsenic pour coprécipiter le sélénium et le tellurium, la dissolution du précipité en acide nitrique dilué et la détermination subséquente du sélénium et du tellurium par spectrophotométrie d'absorption atomique classique. On a mesuré le sélénium et le tellurium de manière courante jusqu'à 0,1 p.p.m.

REFERENCES

1. H. V. Warren and R. E. Delavault, *Proc. Geochem. Expl Symp., 20th Int. Geol. Congress Mexico City*, 1959, 255.
2. H. M. Nakagawa and C. E. Thompson, *U.S. Geol. Surv. Prof. Paper*, 1968, No. 600-B, B 123.
3. B. C. Severne and R. R. Brooks, *Anal. Chim. Acta*, 1972, **58**, 216.
4. G. R. Webber, *Geochim. Cosmochim. Acta*, 1965, **29**, 229.
5. C. E. S. Davis, W. E. Ewers and A. B. Fletcher, *Proc. Australas. Inst. Min. Metall.*, 1969, No. 232, 67.
6. J. H. Watkinson, *Anal. Chem.* ,1966, **38**, 92.
7. J. E. Allan, *Proc. 4th Aust. Spectroscopy Conf., Canberra*, 1963.
8. M. R. Gardiner, J. Armstrong, H. Tels and R. N. Glencross, *Aust. J. Exptl. Ag. Anim. Husb.*, 1962, **2**, 261.

Talanta, 1972, Vol. 19, pp. 1470 to 1474. Pergamon Press. Printed in Northern Ireland

Developments in indicators

(*Received* 30 *September* 1971. *Revised* 11 *February* 1972. *Accepted* 18 *March* 1972)

IN RECENT years narrow-range pH indicators have been introduced.[1,2,3] In addition, a pH indicator changing through three distinct colours has been recommended.[4] α-Aminonaphthaleneazoantipyrine changes from a light colour to a dark one, and then to a light one again.[5] Complementary tristimulus colorimetry has been used for calculating the ratios of the individual components of mixed indicators, necessary for the formation of a transition colour.[6]

Very weak acids which cannot be titrated successfully with alkali in aqueous solution, may be titrated in basic non-aqueous solvents. This approach offers many new possibilities but is also not without some difficulties. Methods are known based on the principle that if the stability constant of a complex is too low, it may be possible to add some substance that will increase the conditional constant.[7] In this way boric acid, which is too weak to be titrated directly, can be transformed into a stronger acid by adding mannitol, and glycine can be titrated after addition of copper sulphate, with Methyl Red as indicator.

Metal–metallochromic indicator complexes can be employed as acid–base indicators, when the formation of a complex is accompanied by the release of more than one proton per indicator molecule. Such an indicator can provide a whole range of pH indicators by variation of the metal ion used.[8]

This paper describes the application of such indicator systems to the titration of weak acids. When an alkali is used as titrant, and a metal indicator together with a metal salt as the acid-base indicator, the colour change occurs at a definite pH, the acid form of the indicator turning not into the alkaline form but into a complex. Some of the possible applications of this principle are illustrated.

1-(2′,4′-Dinitrobenzene)-2-acetyl hydrazine (DBAH) forms green complex with Cu^{2+}, Cu^{+} and to a slight extent with Ni^{2+}. Copper forms a 1:1 complex in aqueous medium; the stability constant was determined spectrophotometrically at pH 8·5 as $\log \beta = 8{\cdot}5$ ($I = 0{\cdot}1$.) The complex is stable at pH 7·8–9·0.[9]

In a conventional acid–base indicator the transition interval is about 2 pH units. In the case of a metal–metallochromic indicator having iminodiacetic acid groups where *n* protons could be released at the same time, the pH interval for the complete colour change would be $2/n$.[8] In the copper–DBAH indicator system the colour change does not occur over a pH range because the complex forms sharply at a definite pH, *e.g.*, at pH 7·62 the colour of the indicator is pale yellow (the complex being not yet formed) but at pH 7·80 the colour is green, being that of the complex.

Figure 1 shows the pH-absorbance curve for the DBAH complex of Cu^{2+}. On the basis of Fig. 1 the p*K* value of DBAH–Cu indicator in the case of $r = 1$ is 7·7. The p*K* value changes relatively only to a slight extent with change in the concentration of the free metal ion present.

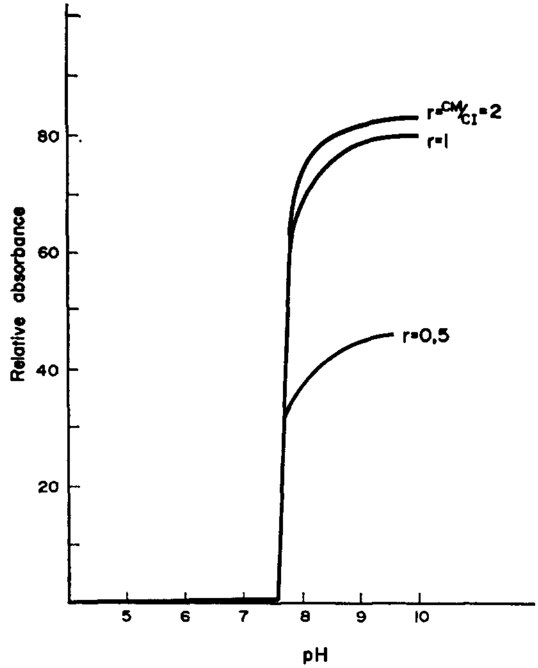


FIG. 1.—The pH-absorbance curve for the DBAH–Cu complex.

Titration of weak acids, using Cu–DBAH *complex as indicator*

Dissolve about 1 mequiv. of benzoic acid in 5 ml of ethanol, add 30 ml of water, 0·2 ml of 0·01*M* (0·024%) ethanolic DBAH, 0·2 ml of 0·01*M* copper sulphate and titrate with 0·1*M* aqueous sodium hydroxide. The acid colour of DBAH is pale yellow, the alkaline one is orange and the copper complex is green. Cu–DBAH complex indicator is not suitable for the titration of weak acids forming complexes with Cu^{2+}, *e.g.*, hydroxycarboxylic acids.

For the titration of weak acids giving a complex with Cu^{2+} as well as having a high p*K* value the magnesium complexes of nitronic acids can be utilized. Azo Violet is a well-known nitronic acid giving a green or blue lake with Mg^{2+} in alkaline medium. The apparent stability constant of the Azo Violet–magnesium complex is $K_{s0}' = 10^{7 \cdot 9}$ and the logarithmic stability constant is $\log K_{s0} = 18{\cdot}26$ at pH 12·10 in sodium hydroxide–glycine buffer.[9]

The magnesium complex of Azo Violet can be used for titrimetric purposes. The precipitation of the complex depends on the alkali and magnesium concentrations. In Fig. 2 the formation of complex is plotted as a function of pH. The formation of the Azo Violet–magnesium complex is not complete, because of the formation of a magnesium hydroxo-complex and magnesium hydroxide.

The colour change occurs here also within a very small pH range, *e.g.*, at pH 11·31 the colour of the indicator is yellow, at pH 11·44 the colour is green (a mixture of the yellow indicator and the blue complex), at pH 11·57 it is blue (the colour of the complex in solution) and at pH 11·8 the blue complex precipitates.

Figure 3 shows the pH transition range for the titration of glycine, as a function of magnesium concentration. The p*K* value of the Azo Violet–magnesium complex indicator corresponds to the pH value for 50% complex formation, $pK_{\mathrm{complex}} = 11{\cdot}45$, which increases with decrease in magnesium concentration.

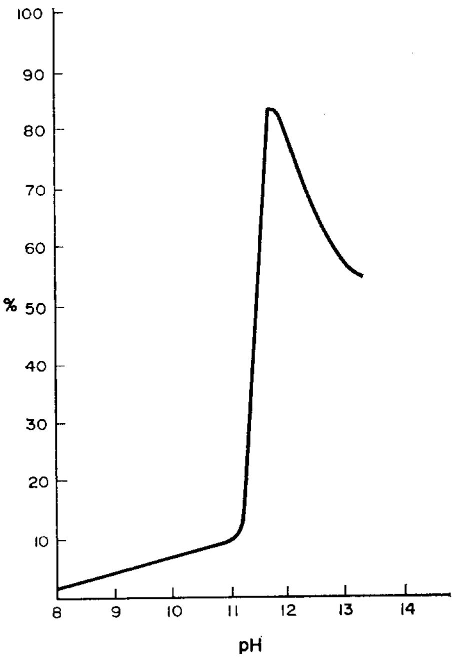


FIG. 2.—Formation of the Mg-Azo Violet complex as a function of pH.

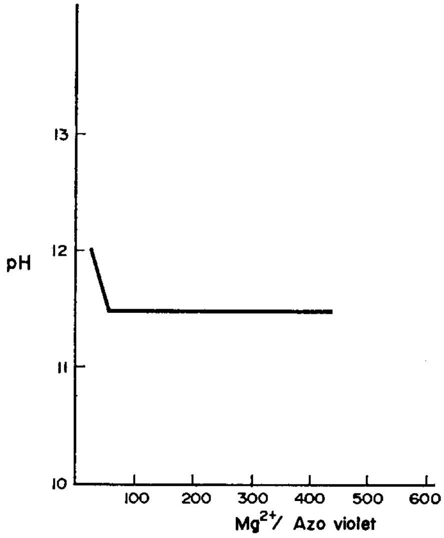


FIG. 3.—Transition pH of titration of glycine, as a function of magnesium concentration.

Titration of weak acids using Azo Violet–magnesium complex as indicator

Dissolve 0·1–0·2 g of glycine in 50 ml of water, add 6 drops of 0·1% acetone solution of Azo Violet, 2 ml of 0·1*M* magnesium sulphate and titrate with 0·1*M* aqueous sodium hydroxide. At the equivalence point the indicator changes its colour from yellow to green. With this indicator system 0·1 g of phenol or of *o*-cresol can be titrated (when 1·5 ml or 0·4 ml of 0·1*M* $MgSO_4$ respectively is added to the Azo Violet). Table I illustrates results obtained with the indicators Cu–DBAH and

Mg–Azo Violet used in titrations with 0·1M sodium hydroxide. For comparison the Cu-DBAH titration was repeated with phenolphthalein as indicator. The absolute error is generally less than 1%. The relative error in the titration of benzoic acid or of glycine is 0·2%. (The volume of 0·1M sodium hydroxide required to raise the pH from 11·31 to 11·44 is 0·5 ml for 70 ml of solution, equivalent to titration of 2 mequiv. of glycine in 50 ml.)

TABLE I.—TITRATION OF WEAK ACIDS (100% PURE).

Acid	Medium	Indicator	Recovery in titration,	
			%	average
Benzoic	aqueous ethanol	Cu-DBAH	100·2	
			100·0	100·2
			100·5	
Benzoic	aqueous ethanol	Phenolphthalein	100·1	
			100·8	100·4
			100·3	
Glycine	water	Mg–Azo Violet	100·3	
			100·4	100·3
			100·1	
			100·5	
Phenol	water	Mg–Azo Violet	99·2	
			99·3	99·4
			99·8	

Nitrokémia Works
Füzfögyártelep
Hungary

L. LÉGRÁDI

Summary—The use of metal ion–metallochromic indicator complexes as narrow-range pH indicators is shown to be advantageous for the titration of weak acids in aqueous media. The Cu–DBAH and the Mg–Azo Violet complexes with apparent pK values of 7·7 and 11·5 have been used for the titrations of benzoic acid and of glycine and phenol, respectively, with good precision.

Zusammenfassung—Es wird gezeigt, daß zur Titration schwacher Säuren in wäßrigen Medien die Verwendung von Komplexen aus Metallionen und Metallfarbindikatoren als Indikatoren für enge pH-Bereiche Vorteile bietet. Die Komplexe Cu-DBAH und Mg-Azoviolett mit scheinbaren pK-Werten von 7,7 und 11,5 wurden für Titrationen von Benzoesäure bzw. von Glycin und Phenol mit guter Genauigkeit verwendet.

Résumé—On montre que l'emploi de complexes ion métallique-indicateur métallochrome comme indicateurs de pH à zone étroite est avantageux pour le titrage d'acides faibles en milieux aqueux. On a utilisé les complexes Cu-DBAH et Mg–Azo Violet avec des valeurs de pK apparentes de 7,7 et 11,5 pour les titrages de l'acide benzoïque, et du glycocolle et du phénol, respectivement, avec une bonne précision.

REFERENCES

1. J. K. Sugden, *Chem. Ind. London*, 1967, 115.
2. M. Singh and J. K. Sugden, *ibid.*, 1968, 845.
3. B. K. Razdan and J. K. Sugden, *ibid.*, 1970, 685.
4. M. Singh and J. K. Sugden, *ibid.*, 1967, 1322.
5. B. Vecerek, Z. Masek and J. Vecerkova, *Chem. Listy*, 1970, **64**, 83.
6. M. Zahradnicek, *Cesk. Farm.*, 1964, **13**, 489.
7. B. Eklund and A. Ringbom, *Finska Kemistsamfundets Medd.*, 1962, **71**, 53.
8. R. A. Chalmers and F. I. Miller, *Analyst*, 1971, **96**, 97.
9. L. Légrádi, *Z. analyt. Chem.* in the press.
10. *Idem*, *Magy. Kem. Folyoirat*, in the press.

Talanta, 1972, Vol. 19, pp. 1474 to 1477. Pergamon Press. Printed in Northern Ireland

Nouvelle microcolorimétrie des nitrites

(*Reçu le* 23 *novembre* 1971. *Accepté le* 5 *avril* 1972)

La littérature scientifique fait état, pour le dosage de faibles quantités d'ion nitrite, de colorimétries obtenues à l'aide de divers réactifs organiques. La plus utilisée, connue sous le nom de Griess,[1–6] est fondée sur la diazotation de l'acide sulfanilique et la copulation du sel de diazonium formé avec la 1-naphthylamine. La sensibilité de la réaction est de l'ordre de 0,01 μg NO_2^-/ml. L'acide sulfanilique diazoté peut, suivant des méthodes voisines, être condensé sur la N-(1-naphthyléthylène diamine)[7] ou le 1-naphthol.[8] D'autres couples de réactifs ont été retenus: *p*-diaminodiphénylsulfone et diphénylamine,[9] acide *p*-sulfanilique et 1-naphthylamine,[10] *p*-nitraniline et guaiazulène,[11] ou azulène,[12] sulfanilamide et N-(1-naphthyléthylène diamine).[13,14] D'autres réactions colorées ont été mises à profit, l'ion nitrite étant révélé entre autres par l'un des réactifs suivants: 2,3-diméthyl 1-phényl pyrazolone,[15] chlorpromazine,[16] Rouge neutre,[17] brucine,[18] strychnine,[19] salipyrine,[20] benzidine.[5]

Nos recherches ont conduit à la mise au point d'une microcolorimétrie fondée sur l'action de l'ion NO_2^- sur l'*o*-tolidine en milieu acétique avec formation d'une coloration jaune à orange. Le tracé et l'étude du spectra d'absorption dans l'ultraviolet et dans le visible (Fig. 1) du colorant formé montrent des maximums vers 206, 280 et 437 nm caractéristiques du groupe azo, suivant les données de la littérature.[21]

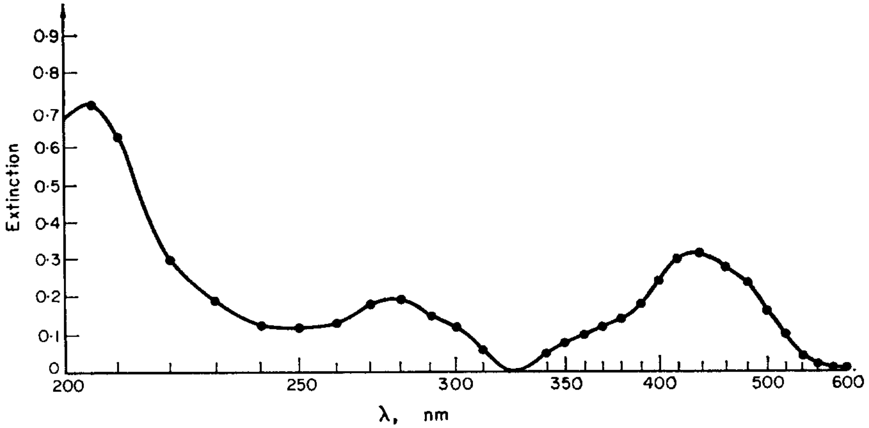


FIG. 1

Les bandes de vibration, caractéristiques du spectre infrarouge à 1460, 970–980 et 750 cm^{-1} ne sont pas en désaccord avec cette donnée, les bandes 3350 et 3450 cm^{-1} identifiant un groupe

REFERENCES

1. J. K. Sugden, *Chem. Ind. London*, 1967, 115.
2. M. Singh and J. K. Sugden, *ibid.*, 1968, 845.
3. B. K. Razdan and J. K. Sugden, *ibid.*, 1970, 685.
4. M. Singh and J. K. Sugden, *ibid.*, 1967, 1322.
5. B. Vecerek, Z. Masek and J. Vecerkova, *Chem. Listy*, 1970, **64**, 83.
6. M. Zahradnicek, *Cesk. Farm.*, 1964, **13**, 489.
7. B. Eklund and A. Ringbom, *Finska Kemistsamfundets Medd.*, 1962, **71**, 53.
8. R. A. Chalmers and F. I. Miller, *Analyst*, 1971, **96**, 97.
9. L. Légrádi, *Z. analyt. Chem.* in the press.
10. *Idem*, *Magy. Kem. Folyoirat*, in the press.

Talanta, 1972, Vol. 19, pp. 1474 to 1477. Pergamon Press. Printed in Northern Ireland

Nouvelle microcolorimétrie des nitrites

(*Reçu le* 23 *novembre* 1971. *Accepté le* 5 *avril* 1972)

LA LITTÉRATURE scientifique fait état, pour le dosage de faibles quantités d'ion nitrite, de colorimétries obtenues à l'aide de divers réactifs organiques. La plus utilisée, connue sous le nom de Griess,[1–6] est fondée sur la diazotation de l'acide sulfanilique et la copulation du sel de diazonium formé avec la 1-naphthylamine. La sensibilité de la réaction est de l'ordre de 0,01 μg NO_2^-/ml. L'acide sulfanilique diazoté peut, suivant des méthodes voisines, être condensé sur la N-(1-naphthyléthylène diamine)[7] ou le 1-naphthol.[8] D'autres couples de réactifs ont été retenus: *p*-diaminodiphénylsulfone et diphénylamine,[9] acide *p*-sulfanilique et 1-naphthylamine,[10] *p*-nitraniline et guaiazulène,[11] ou azulène,[12] sulfanilamide et N-(1-naphthyléthylène diamine).[13,14] D'autres réactions colorées ont été mises à profit, l'ion nitrite étant révélé entre autres par l'un des réactifs suivants: 2,3-diméthyl 1-phényl pyrazolone,[15] chlorpromazine,[16] Rouge neutre,[17] brucine,[18] strychnine,[19] salipyrine,[20] benzidine.[5]

Nos recherches ont conduit à la mise au point d'une microcolorimétrie fondée sur l'action de l'ion NO_2^- sur l'*o*-tolidine en milieu acétique avec formation d'une coloration jaune à orange. Le tracé et l'étude du spectra d'absorption dans l'ultraviolet et dans le visible (Fig. 1) du colorant formé montrent des maximums vers 206, 280 et 437 nm caractéristiques du groupe azo, suivant les données de la littérature.[21]

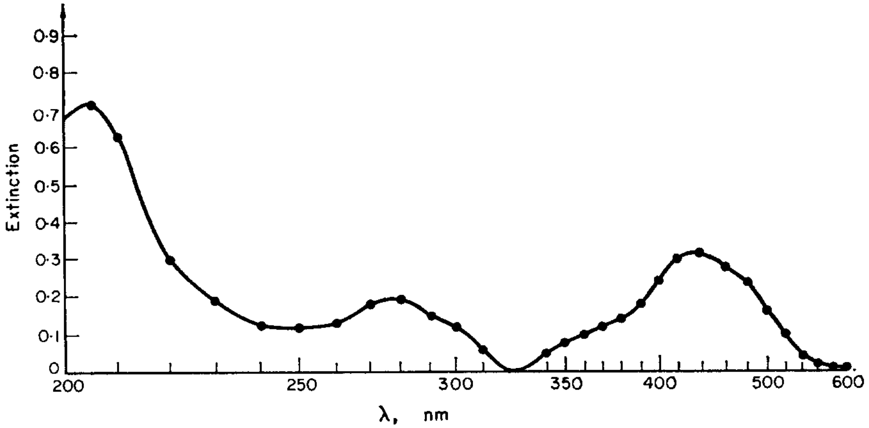
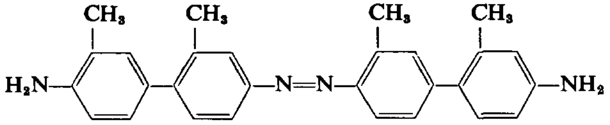


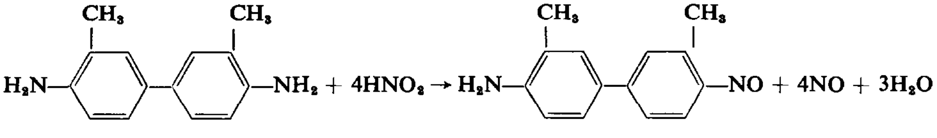
FIG. 1

Les bandes de vibration, caractéristiques du spectre infrarouge à 1460, 970–980 et 750 cm^{-1} ne sont pas en désaccord avec cette donnée, les bandes 3350 et 3450 cm^{-1} identifiant un groupe amino. Avançant l'hypothèse de la structure suivante (I) pour le composé formé

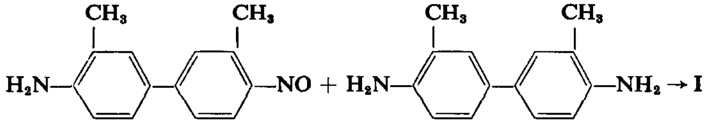


(I)

on peut supposer dans un premier temps l'oxydation de l'*o*-tolidine avec formation d'un dérivé nitrosé[22]



puis la réaction de celui-ci sur une autre molécule d'*o*-tolidine



La colorimétrie des nitrites par l'*o*-tolidine est perturbée par la présence de divers ions: $Cr_2O_7^{2-}$(>1 μg/ml), Cu^{2+}(>500 μg/ml), Fe^{3+}(>100 μg/ml), IO_3^-(>20 μg/ml), IO_4^-($>0,5$ μg/ml), avec formation d'une coloration bleue. D'autres ions apportent également une gêne UO_2^{2+}(>1 μg/ml), $Sb_2O_7^{2-}$(>1 μg/ml) = coloration jaune.

Le pH optimum pour effectuer la réaction est compris entre 3,5 et 4,5 ainsi que le montrent les variations de l'extinction en fonction du pH (Tableau I).

TABLEAU I.—L'EXTINCTION EN FONCTION DE pH.

NO_2^-, μg	pH							
	2,5	3,0	3,5	4,0	4,5	5,0	5,5	6,0
0,5	0,015	0,026	0,034	0,034	0,035	0,041	0,055	0,072
1,0	0,054	0,060	0,069	0,070	0,070	0,073	0,081	0,106
3,0	0,182	0,190	0,213	0,216	0,214	0,230	0,242	0,256
6,0	0,372	0,402	0,432	0,431	0,434	0,445	0,463	0,495
8,0	0,495	0,550	0,579	0,582	0,590	0,596	0,608	0,635
10,0	0,632	0,703	0,720	0,721	0,723	0,735	0,743	0,870

PARTIE EXPERIMENTALE

Réactifs

Solution mère de NO_2Na contenant 0,3728 g de nitrite de sodium pour 250 ml (1 ml $\equiv$ 1 mg NO_2^-). La solution, conservée en verre jaune, est stable plusieurs mois.

Solutions diluées de NO_2Na obtenues par dilution extemporanée de la solution mère pour obtenir 0,25–10 μg NO_2^-/ml. La stabilité n'excède pas quelques jours.

Solution d'o-tolidine obtenue en dissolvant 1 g d'*o*-tolidine purifiée dans 10 ml d'acide acétique pur et diluant à 100 ml avec de l'eau. Conservée en verre jaune, la solution est stable pendant deux mois.

Solution de fluorure d'ammonium; solution aqueuse à 10%.

Gamme d'étalonnage

A 1 ml des solutions diluées de NO_2Na soit 0,25–10 μg NO_2^-, on ajoute 1 ml de solution de fluorure d'ammonium, 1 ml de solution d'*o*-tolidine et complète à 5 ml avec de l'eau. Lecture à 437 nm en cuve de 1 cm après 10 minutes (la coloration est stable jusqu'à 40 minutes après réaction).

Dosage des nitrites dans les eaux potables et les eaux minérales

L'eau à analyser (10–50 ml) est placé dans une capsule de verre, neutralisé et évaporé à sec au bain-marie. Le résidu est repris par 3 ml d'eau puis on ajoute 1 ml de solution de fluorure d'ammonium, 1 ml de solution d'*o*-tolidine. Lecture après 10 minutes à 437 nm après centrifugation éventuelle et report à la courbe d'étalonnage. Plusieurs résultats sont consignés dans le Tableau II, montrant que l'erreur relative moyenne est ±1% ainsi que la comparaison avec la méthode par diazocopulation solon Greiss.

TABLEAU II.

Prise d'essai, *ml*	NO_2^- ajouté *μg*	NO_2^- trouvé *μg*	Différence *μg*	Erreur relative, %	*μg* NO_2^-/100 *ml* méthode a l'*o*-tolidine	*μg* NO_2^-/100 *ml* méthode de Greiss
15,00	—	1,62	—	—	10,8	10,2
15,00	1,00	2,62	0,00	−0,0	—	—
25,00	—	2,45	—	—	9,8	10,0
25,00	1,00	3,50	0,05	+2,0	—	—
25,00	—	2,50	—	—	10,0	10,2
25,00	2,00	4,52	0,02	+0,8	—	—

Laboratoie de Chimie Analytique
de la Faculté de Pharmacie de Iassy
Roumanie

CAMELIA GHIMICESCU
VASILE DORNEANU

Résumé—On propose, pour la détermination des nitrites, une microméthode fondée sur une réaction avec l'*o*-tolidine, avec formation d'un composé azoïque coloré en jaune-orange, permettant la spectrophotométrie. La sensibilité de la réaction est de 0,05 *μg* NO_2^-/ml. La méthode est applicable à la détermination des nitrites dans les eaux potables et les eaux minérales, avec une erreur relative moyenne de ±1%.

Summary—A micromethod for determination of nitrite is based on a reaction with *o*-tolidine, forming a yellow-orange product suitable for spectrophotometry. The sensitivity is 0·05 *μg* of nitrite/ml. The method is suitable for analysis of potable and mineral waters, and has a mean relative error of 1%.

Zusammenfassung—Eine Mikromethode zur Bestimmung von Nitrit beruht auf der Reaktion mit o-Tolidin, wobei sich ein für die Spektralphotometrie geeignetes gelb-orangefarbiges Produkt bildet. Die Empfindlichkeit beträgt 0,05 *μg* Nitrit/ml. Die Methode ist zur Analyse von Trink- und Mineralwasser geeignet und weist einen mittleren relativen Fehler von 1% auf.

BIBLIOGRAPHIE

1. N. S. Drozdov et A. K. Iskandrajn, *Zh. Analit. Khim.*, 1957, **11**, 723.
2. F. Feigl, *Tüpfelanalyse*, p. 333, 1960.
3. P. Griess, *Ber.*, 1879, **12**, 427.
4. A. Jolles, *Z. Anal. Chem.*, 1893, **32**, 763.
5. G. Lunge, *Angew. Chem.*, 1889, **2**, 666.
6. D. F. Boltz, *Colorimetric Determination of Nonmetals*, Interscience, New York, 1958.
7. B. E. Saltzman, *Anal. Chem.*, 1954, **26**, 1949.

8. W. A. Landmann, *J. Assoc. Offic. Anal. Chemists*, 1966, **49**, 875.
9. E. Szekely, *Talanta*, 1968, **15**, 795.
10. B. F. Rider et M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 96.
11. A. Lembek et O. Moebus, *Milchwissenschaft*, 1968, **23**, 211.
12. E. E. Garcia, *Anal. Chem.*, 1967, **39**, 1605.
13. A. C. Bratton et E. K. Marshall, *J. Biol. Chem.*, 1939, **128**, 537.
14. M. B. Jacobs et S. Hochheiser, *Anal. Chem.*, 1958, **30**, 426.
15. F. Bermejo-Martinez et M. Zunzunegui-Perez, *Inf. Quim. Anal. (Madrid)*, 1968, **22**, 13.
16. A. Kieruczenkowa, *Farm. Polsk.*, 1966, **22**, 283.
17. M. V. Alekseeva et S. S. Gurvits, *Chim. Ind. (Paris)*, 1938, **39**, 474.
18. F. L. Fisher, E. R. Berl et H. F. Beckman, *Anal. Chem.*, 1958, **30**, 1972.
19. F. J. Welcher, *Organic Analytical Reagents* Vol. IV. Van Nostrand, New York, 1961.
20. Gh. Ghimicescu, *Ann. Sci. Univ. Iassy*, 1935, **21**, 330.
21. I. Reichel, *Chimia çi technologia coloranţilor azoici*, Ed. Acad. R.S.R., 1955.
22. Houben Weyl, *Methoden der Organischen Chemie*, Bd XI/2, 182.

Talanta, 1972, Vol. 19, pp. 1477 to 1478. Pergamon Press. Printed in Northern Ireland

Analytical application of the urease method for determination of urea in the presence of biuret

(*Received* 25 *August* 1970. *Revised* 8 *March* 1972. *Accepted* 1 *May* 1972)

It is well known that urease acts on urea to catalyse the reaction

$$CO(NH)_2 + 2H_2O = (NH_4)_2CO_3$$

and a method for determination of urea has been developed on the basis of this reaction.

Many opinions have been published regarding the specificity of the reaction. According to some authors the urease also acts on biuret,[1] according to others the activity of urease towards biuret is only apparent and is due to small amounts of urea in the biuret.[2]

Our preliminary investigations showed that the pH of a solution of pure biuret does not change during more than an hour in the presence of crystal urease or an alcoholic extract of the enzyme. It was therefore decided that mixtures of urea and biuret could be analysed according to the procedure described in the literature.[3]

EXPERIMENTAL

An alcoholic extract of urease was prepared from soya beans.[3] A mixture of urea and phosphorus pentoxide was heated at about 90°. The products of the reaction[4] contain nitrogen in various forms, which can be determined by appropriate methods: total nitrogen—according to Kjeldahl;[3] ammonia nitrogen—according to ref. 5; urea nitrogen—according to the procedure given in ref. 3; biuret nitrogen—by the colorimetric method.[6]

All reagents were of analytical grade.

RESULTS AND DISCUSSION

A series of solutions was prepared containing different ratios of urea and biuret (Table I). It was found that the alcoholic extract of urease catalyses the hydrolysis reaction of the urea and not that of the biuret.

Table I.—Effect of biuret on the determination of urea by the urease method.

Urea, %	Biuret, %	Urea nitrogen, % calculated	Urea nitrogen, % found
0	100	0·0	0·0
25	75	11·6	11·6
50	50	23·2	23·2
75	25	34·9	34·7
100	0	46·5	46·5

8. W. A. Landmann, *J. Assoc. Offic. Anal. Chemists*, 1966, **49**, 875.
9. E. Szekely, *Talanta*, 1968, **15**, 795.
10. B. F. Rider et M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 96.
11. A. Lembek et O. Moebus, *Milchwissenschaft*, 1968, **23**, 211.
12. E. E. Garcia, *Anal. Chem.*, 1967, **39**, 1605.
13. A. C. Bratton et E. K. Marshall, *J. Biol. Chem.*, 1939, **128**, 537.
14. M. B. Jacobs et S. Hochheiser, *Anal. Chem.*, 1958, **30**, 426.
15. F. Bermejo-Martinez et M. Zunzunegui-Perez, *Inf. Quim. Anal. (Madrid)*, 1968, **22**, 13.
16. A. Kieruczenkowa, *Farm. Polsk.*, 1966, **22**, 283.
17. M. V. Alekseeva et S. S. Gurvits, *Chim. Ind. (Paris)*, 1938, **39**, 474.
18. F. L. Fisher, E. R. Berl et H. F. Beckman, *Anal. Chem.*, 1958, **30**, 1972.
19. F. J. Welcher, *Organic Analytical Reagents* Vol. IV. Van Nostrand, New York, 1961.
20. Gh. Ghimicescu, *Ann. Sci. Univ. Iassy*, 1935, **21**, 330.
21. I. Reichel, *Chimia çi technologia coloranţilor azoici*, Ed. Acad. R.S.R., 1955.
22. Houben Weyl, *Methoden der Organischen Chemie*, Bd XI/2, 182.

Talanta, 1972, Vol. 19, pp. 1477 to 1478. Pergamon Press. Printed in Northern Ireland

Analytical application of the urease method for determination of urea in the presence of biuret

(*Received* 25 *August* 1970. *Revised* 8 *March* 1972. *Accepted* 1 *May* 1972)

IT IS WELL KNOWN that urease acts on urea to catalyse the reaction

$$CO(NH)_2 + 2H_2O = (NH_4)_2CO_3$$

and a method for determination of urea has been developed on the basis of this reaction.

Many opinions have been published regarding the specificity of the reaction. According to some authors the urease also acts on biuret,[1] according to others the activity of urease towards biuret is only apparent and is due to small amounts of urea in the biuret.[2]

Our preliminary investigations showed that the pH of a solution of pure biuret does not change during more than an hour in the presence of crystal urease or an alcoholic extract of the enzyme. It was therefore decided that mixtures of urea and biuret could be analysed according to the procedure described in the literature.[3]

EXPERIMENTAL

An alcoholic extract of urease was prepared from soya beans.[3] A mixture of urea and phosphorus pentoxide was heated at about 90°. The products of the reaction[4] contain nitrogen in various forms, which can be determined by appropriate methods: total nitrogen—according to Kjeldahl;[3] ammonia nitrogen—according to ref. 5; urea nitrogen—according to the procedure given in ref. 3; biuret nitrogen—by the colorimetric method.[6]

All reagents were of analytical grade.

RESULTS AND DISCUSSION

A series of solutions was prepared containing different ratios of urea and biuret (Table I). It was found that the alcoholic extract of urease catalyses the hydrolysis reaction of the urea and not that of the biuret.

TABLE I.—EFFECT OF BIURET ON THE DETERMINATION OF UREA BY THE UREASE METHOD.

Urea, %	Biuret, %	Urea nitrogen, %	
		calculated	found
0	100	0·0	0·0
25	75	11·6	11·6
50	50	23·2	23·2
75	25	34·9	34·7
100	0	46·5	46·5

The analytical application of the urease method was verified by analysis of the products of the reaction of the mixture of phosphorus pentoxide and urea heated at about 90° (Table II). The results for the biuret nitrogen found by the colorimetric method compare favourably with those calculated.

TABLE II.—DETERMINATION OF NITROGEN IN PRODUCTS OBTAINED BY HEATING A MIXTURE OF UREA AND PHOSPHORUS PENTOXIDE.

Nitrogen, %				
Total	Ammonia	Urea	Biuret	
			calculated	found
31·4	2·4	22·1	6·9	6·9
35·1	1·2	29·3	4·6	4·5
37·6	1·9	29·0	6·7	6·7

Chemico-Technological Institute
Sofia 56, Bulgaria

P. BOZADZIEV
E. BALABANOVA
L. ILCHEVA

Summary—Biuret does *not* interfere in the urease-catalysed hydrolysis of urea.

Zusammenfassung—Biuret stört nicht bei der Urease-katalysierten Hydrolyse von Harnstoff.

Résumé—Le biuret n'interfère pas dans l'hydrolyse de l'urée catalysée par l'uréase.

REFERENCES

1. F. Feigl, *Kapelnii Analiz Organicheskih Veshtestv*, p. 594. Moscow. 1962,
2. J. E. Varner, *The Enzymes*, 4, p. 247, Academic Press, New York 1960.
3. M. V. Katalimova, ed. *Spravochnik po Mineralnim Udobrenijam*, p. 455. Moscow, 1960.
4. P. Bozadziev, C. Volfkovich, A. Chehovskih, *Zh. Prikl. Khim.*, 1967, **40**, 895.
5. K. Massuryan, *Nauch, Agrokhim. Zh.*, 1929, 7.
6. L. H. Sverak, *Z. Anal. Chem.*, 1959, **169**, 178.

Talanta, 1972, Vol. 19, pp. 1478 to 1480. Pergamon Press. Printed in Northern Ireland

Determination of gallium in an iron-aluminium matrix by solvent extraction and flame emission spectroscopy

(*Received* 7 *March* 1972. *Accepted* 15 *May* 1972)

GALLIUM is readily determined by flame emission spectroscopy (FES) in a variety of flames, and under optimized conditions this technique has been shown to give detection limits superior to those obtainable by atomic-absorption spectroscopy.[1] The application of FES to the determination of gallium in matrices such as soil or rock fusion fluxes, which may contain very substantial excesses of iron and aluminium, is limited[1,2] by the increase in background emission attributable to the concomitant elements, even when a spectral band-pass as low as 0·04 nm is employed.[2] For aqueous solutions, extraction of the 8-quinolinolate[3,4] or pyrollidinedithiocarbamate[5] has been recommended as a preconcentration technique before flame spectroscopic analysis, and the addition of organic solvents has been suggested[6] as a method of enhancing the sensitivity of the determination. Methods commonly used[7] for the extraction of gallium are susceptible to co-extraction of iron(III), however. Sandell overcame[8] this problem by reduction of iron(III) to iron(II) by filtration through silver powder, The analytical application of the urease method was verified by analysis of the products of the reaction of the mixture of phosphorus pentoxide and urea heated at about 90° (Table II). The results for the biuret nitrogen found by the colorimetric method compare favourably with those calculated.

TABLE II.—DETERMINATION OF NITROGEN IN PRODUCTS OBTAINED BY HEATING A MIXTURE OF UREA AND PHOSPHORUS PENTOXIDE.

Nitrogen, %				
Total	Ammonia	Urea	Biuret	
			calculated	found
31·4	2·4	22·1	6·9	6·9
35·1	1·2	29·3	4·6	4·5
37·6	1·9	29·0	6·7	6·7

Chemico-Technological Institute
Sofia 56, Bulgaria

P. BOZADZIEV
E. BALABANOVA
L. ILCHEVA

Summary—Biuret does *not* interfere in the urease-catalysed hydrolysis of urea.

Zusammenfassung—Biuret stört nicht bei der Urease-katalysierten Hydrolyse von Harnstoff.

Résumé—Le biuret n'interfère pas dans l'hydrolyse de l'urée catalysée par l'uréase.

REFERENCES

1. F. Feigl, *Kapelnii Analiz Organicheskih Veshtestv*, p. 594. Moscow. 1962,
2. J. E. Varner, *The Enzymes*, 4, p. 247, Academic Press, New York 1960.
3. M. V. Katalimova, ed. *Spravochnik po Mineralnim Udobrenijam*, p. 455. Moscow, 1960.
4. P. Bozadziev, C. Volfkovich, A. Chehovskih, *Zh. Prikl. Khim.*, 1967, **40**, 895.
5. K. Massuryan, *Nauch, Agrokhim. Zh.*, 1929, 7.
6. L. H. Sverak, *Z. Anal. Chem.*, 1959, **169**, 178.

Talanta, 1972, Vol. 19, pp. 1478 to 1480. Pergamon Press. Printed in Northern Ireland

Determination of gallium in an iron–aluminium matrix by solvent extraction and flame emission spectroscopy

(*Received* 7 *March* 1972. *Accepted* 15 *May* 1972)

GALLIUM is readily determined by flame emission spectroscopy (FES) in a variety of flames, and under optimized conditions this technique has been shown to give detection limits superior to those obtainable by atomic-absorption spectroscopy.[1] The application of FES to the determination of gallium in matrices such as soil or rock fusion fluxes, which may contain very substantial excesses of iron and aluminium, is limited[1,2] by the increase in background emission attributable to the concomitant elements, even when a spectral band-pass as low as 0·04 nm is employed.[2] For aqueous solutions, extraction of the 8-quinolinolate[3,4] or pyrollidinedithiocarbamate[5] has been recommended as a preconcentration technique before flame spectroscopic analysis, and the addition of organic solvents has been suggested[6] as a method of enhancing the sensitivity of the determination. Methods commonly used[7] for the extraction of gallium are susceptible to co-extraction of iron(III), however. Sandell overcame[8] this problem by reduction of iron(III) to iron(II) by filtration through silver powder, followed by the immediate extraction of the gallium chloro-complex into diethyl ether from hydrochloric acid solution. The method described here involves the use of titanous sulphate as a reductant, which obviates the need for filtration and, by maintaining a reducing environment, for immediate extraction. Methyl isobutyl ketone,[9] which is a particularly suitable solvent[4] for the flame spectroscopic determination of gallium, is employed as an extractant.

EXPERIMENTAL

Reagents

Gallium(III) *solution*, 1·00 mg/ml Dissolve 1·00 g of gallium metal in the minimum necessary volume of reagent-grade constant-boiling hydrochloric acid; dilute to 1 litre.

Diverse ions. Stock solutions were prepared for a range of elements from the metals as above, or from suitable metal salts.

Titanium(III) *sulphate solution, 15% w/v.*

Apparatus

Flame emission/atomic absorption spectrometer. A Unicam model SP900A with 5-cm air–acetylene slot-burner was used in the emission mode.

Procedure

Evaluation of the effect of hydrochloric acid concentration on extraction efficiency. Twenty-ml aliquots of 50 μg/ml gallium solutions in hydrochloric acid (0–6*M w.r.t.* HCl in final solution) were extracted with 5 ml of methyl isobutyl ketone. The organic phases were nebulized into a fuel-lean air–acetylene flame, and the intensity of the gallium emission at 417·2 nm was measured.

Procedure in the presence of large excesses of Fe(III) and Al(III). To suitable aliquots of neutral or near neutral test solutions and standards, were added 10 ml of concentrated hydrochloric acid and 2 ml of titanium(III) sulphate solution. The solutions were diluted to 20 ml, shaken, and extracted with 5 ml of methyl isobutyl ketone. The emission intensity was measured for the organic phase, methyl isobutyl ketone previously saturated with hydrochloric acid being used to set the instrumental zero. Linear calibration curves could be prepared over the range 0–1 and 0–12 μg/ml (gallium concentration in aqueous phase). The variation in standard deviation and related parameters with gallium concentration (based on ten determinations) is shown in Table I.

RESULTS AND DISCUSSION

Figure 1 illustrates the effect of acid concentration on the gallium emission intensity. Acid digestions of 5-ml aliquots of organic phase, and evaporation of 10-ml aliquots of aqueous phase to dryness followed by dissolution of any residue in 10 ml of 1*M* hydrochloric acid, indicated quantitative extraction of gallium over the acid concentration range 4·3–7·2*M*, within the limits of experimental error (i.e. >98% extraction). Over this acid concentration range, atomic-absorption spectroscopic analysis indicated that iron(III) was virtually quantitatively co-extracted, whereas aluminium was not extracted to any measurable extent. The interference of iron(III) was found to be eliminated by reduction to iron(II) with titanous sulphate. This procedure was found to be effective in dealing with 5000-fold excesses (the largest investigated) of iron in the determination of gallium concentration

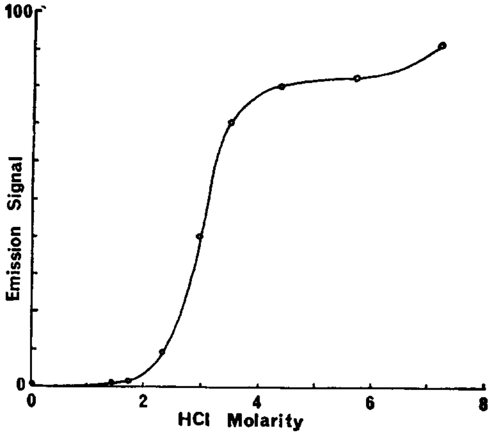


Fig. 1.—The influence of hydrochloric acid concentration on the emission signal from 50-μg/ml gallium solutions after extraction into methyl isobutyl ketone.

TABLE I.—PRECISION OF RESULTS.

Gallium concentration, *μg/ml*	Signal range	Mean signal	Standard deviation	Relative standard deviation, %
1·0	72–80	77·7	0·9	1
0·2	10–20·5	16·0	1·0	6
0·05	−1–8·5	4·0	1·0	25

of 2 μg/ml in aqueous solution, *i.e.*, 0·5 μg/ml in the aqueous phase when using a 5-ml aliquot for analysis. Thousand-fold excesses of the following elements caused no measurable interference in the determination of the same concentration of gallium; Al, Ba, Ca, Cd, Co, Cr, K, La, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, Tl, V and Zn; copper, which is partially co-extracted under these conditions, was found to give rise to appreciable spectral interference. At the level mentioned, which is at least an order of magnitude greater than that likely to be encountered in soil samples, this caused a 50% enhancement in the gallium signal.

To obtain some indication of the influence of other acids likely to be encountered after digestion procedures, on the determination of gallium at the 50 μg/ml level, solutions were prepared which were 5·7*M* with respect to hydrochloric acid, and also 2·0*N* with respect to sulphuric, nitric and perchloric acid: At this level sulphuric acid gave an enhancement of 3%, whereas nitric and perchloric acids caused suppressions of 62% and 77% respectively. Although the interference of nitric and perchloric acids may be ignored provided samples and standards are carefully matched with respect to acid concentration, both acids were found to impede the quantitative reduction of iron(III) to iron(II) with titanium(III) sulphate. The result obtained for sulphuric acid indicates that the sulphuric acid content of the titanium(III) sulphate solution is not critical.

Department of Soil Science
University of Aberdeen
Scotland

M. S. CRESSER
J. TORRENT-CASTELLET

Summary—Solvent extraction of gallium(III) into methyl isobutyl ketone from hydrochloric acid solutions containing titanium(III) sulphate provides a rapid method for separation of gallium from an iron/aluminium matrix and may be employed to eliminate the interference of these elements in the flame emission spectrometric determination of gallium.

Zusammenfassung—Lösende Ausscheidung von Gallium(III) in Methylisobutylketon aus Salzsäurelösungen mit Titanium(III) Sulphatgehalt stellt eine schnelle Methode zur Trennung von Gallium aus einer Eisen/Aluminium-Grundmasse dar und kann benutzt werden, die Interferenz dieser Elemente bei der Flammenausstrahlung spektrometrischer Ermittlung von Gallium zu eliminieren.

Résumé—L'extraction par solvant du gallium(III) en méthylisobutylcétone à partir de solutions en acide chlorhydrique contenant du sulfate de titane(III) fournit une méthode rapide pour la séparation du gallium d'une matrice fer/aluminium et peut être employée pour éliminer l'interference de ces éléments dans le dosage spectrométrique du gallium par émission de flamme.

REFERENCES

1. E. E. Pickett and S. R. Koirtyohann, *Spectrochim. Acta*, 1969, **24B**, 325.
2. U. W. Meloche and B. L. Beck, *Anal. Chem.*, 1956, **28**, 1890.
3. E. Sudo and H. Goto, *Sci. Rept. Res. Inst. Tohoku Univ., Ser. A*, 1962, **14**, 220, *Chem. Abstr.* 1963, **58**, 5030.
4. *Idem*, *Trans. Natl. Res. Inst. Metals* (*Tokyo*) 1963, **5**, 158; *Chem. Abstr.* 1964, **60**, 3481.
5. C. E. Mulford, *At. Abs. Newsletter*, 1966, **5**, 88.
6. K. H. Neeb, *Z. Anal. Chem.* 1961, **184**, 414.
7. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry.* Wiley, New York, 1957.
8. E. B. Sandell, *Anal. Chem.*, 1947, **19**, 63.
9. Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes.* Wiley-Interscience, New York, 1969.

Talanta, 1972, Vol. 19, pp. 1481 to 1482. Pergamon Press. Printed in Northern Ireland

ANALYTICAL DATA

Complexes of some rare earth metals with 1-amino-4-hydroxyanthraquinone

(*Received* 7 *February* 1972. *Accepted* 5 *March* 1972)

THE FLUORESCENCE SPECTRA of beryllium and thorium-1-amino-4-hydroxy-anthraquinone complexes were studied by White *et al.*,[1] but no systematic study has been made of the complexes of 1-amino-4-hydroxyanthraquinone with metal ions. The present paper deals with the lanthanum, cerium, praseodymium, neodymium and samarium complexes.

EXPERIMENTAL

Reagents

1-*Amino*-4-*hydroxyanthraquinone* (*AHA*). The reagent was prepared by the direct condensation of phthalic anhydride and triacetyl *p*-aminophenol in the presence of an anhydrous aluminium chloride–sodium chloride melt.[2] The product was purified by thin-layer and column chromatography, and used as a solution in methanol.

Lanthanide chloride solutions. Prepared as methanol solutions.

Nature of the complex

AHA immediately gives a reddish-violet colour with La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}. The colour remains unchanged for 3 or 4 days.

Vosburgh and Cooper's method[3] showed that only one type of complex was formed. The absorption maximum was at 530 nm for AHA and at 605 nm for La, Pr and Sm and 610 nm for Ce and Nd.

The method of continuous variations,[4] mole-ratio,[5] and slope ratio[6] methods all showed the complexes to be 1:1.

Evaluation of stability constants

The stability constants were determined from the absorbances measured in the Job's method by using Banerji and Dey's formula[7]

$$K = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

where a_1 and a_2 are the total concentrations of metal, b_1 and b_2 the total concentrations of AHA and x the concentration of the complex at equilibrium.

TABLE I.—STABILITY CONSTANTS AND FREE ENERGY OF FORMATION OF VARIOUS METAL–AHA COMPLEXES AT 30°C.

Complex	λ_{max} nm	$\log K$	Method	ΔG^0, *kcal/mole*
La(III)–AHA	605	5·16 ± 0·08	(a)	—
		5·26 ± 0·02	(b)	7·34 ± 0·03
Ce(III)–AHA	610	5·25 ± 0·10	(a)	—
		5·33 ± 0·03	(b)	7·40 ± 0·02
Pr(III)–AHA	605	5·36 ± 0·08	(a)	—
		5·42 ± 0·04	(b)	7·57 ± 0·05
Nd(III)–AHA	610	5·40 ± 0·14	(a)	—
		5·45 ± 0·03	(b)	7·60 ± 0·04
Sm(III)–AHA	605	5·25 ± 0·06	(a)	—
		5·46 ± 0·04	(b)	7·62 ± 0·06

(a) Banerji and Dey method.[7]
(b) Mole-ratio method.

The mole-ratio method was also used by means of the equation

$$K = \frac{1 - \alpha}{\alpha^2 C}$$

where C is the concentration of the complex and α is the degree of dissociation, given by

$$\alpha = \frac{A_m - A_s}{A_m}$$

where A_m is the absorbance of the complex when excess of AHA is present and A_s is the absorbance of the complex at the equivalence point.

The free energy of formation was calculated from K. The results are summarized in Table I. The stability constants are very similar, increasing as the size of the cation decreases.

Acknowledgement—The authors are grateful to Prof. R. C. Kapoor, Head of the Chemistry Department for providing the necessary facilities.

Chemical Laboratories
University of Jodhpur
Jodhpur, India

A. K. JAIN✠
V. P. AGGARWALA
PURAN CHAND
S. P. GARG*

Summary—La, Ce(III), Pr, Nd and Sm(III) form very stable reddish-violet 1:1 complexes with 1-amino-4-hydroxyanthraquinone in methanol. The stability constants are very similar.

Zusammenfassung—La, Ce(III), Pr, Nd und Sm(III) bilden mit 1-Amino-4-Hydroxylanthrachinon in Methanol sehr beständige rötlich-violette 1:1 Komplexverbindungen. Die Resistenzkonstanten sind sehr ähnlich.

Résumé—La, Ce(III), Pr, Nd et Sm(III) forment des complexes violet-rougeâtres 1:1 très stables avec la 1-amino 4-hydroxyanthraquinone en méthanol. Les constantes de stabilité sont très similaires.

REFERENCES

1. M. H. Fletcher, C. E. White and M. S. Sheftel, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 179.
2. V. P. Aggarwala, *Ph.D. Thesis*, University of Jodhpur, India, 1971.
3. W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, 1941, **63**, 437.
4. P. Job, *Ann. Chim. (Paris)*, 1928, **9**, 113.
5. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 111.
6. A. Harvey and D. Manning, *J. Am. Chem. Soc.*, 1950, **72**, 4488.
7. S. K. Banerji and A. K. Dey, *Z. Anal. Chem.*, 1961, **30**, 179.

Talanta, 1972 Vol. 19, pp. 1483 to 1486. Pergamon Press. Printed in Northern Ireland

ANNOTATIONS

A study of the evaporation of gold solutions

(*Received* 2 *March* 1972. *Accepted* 26 *March* 1972)

There have been several reports in the literature, referring to losses of gold by volatilization on heating of gold solutions. Mizuike and Takata[1] reported the loss of the trace elements ^{51}Cr, ^{60}Co, ^{65}Zn, ^{110}Ag, ^{198}Au and ^{203}Hg when solutions were evaporated to dryness at 100°. Gilchrist[2] found as much as 2% loss of gold as gold chloride upon heating to dryness, presumably through volatilization. On the other hand, some authors have not considered the possibility of gold losses. Plaskin and Kayukhova[3] did not consider gold losses in their determination of gold by hydrazine hydrochloride, which involved repeated evaporation with hydrochloric acid at temperatures not over 60–70°. In co-crystallization experiments with 2-mercaptobenzimidazole, Weiss and Lai[4] did not consider the possibility of gold volatilization occurring during the several hours of boiling required. A colorimetric method by Brodigan[5] ignored any loss of gold during an evaporation to a volume of 1–2 ml. The colorimetric method by Gachev[6] required the boiling of a gold solution to dryness but gave no consideration to any possible gold loss. Novikova[7] showed that the process of dissolving gold is temperature-dependent but did not discuss possible gold losses.

Chapman, Marvin and Tyree[8] reported specifically on the volatilization of elements in solutions of mixed hydrofluoric and perchloric acids heated to dryness by an overhead heating unit kept at 200°. They concluded that under these conditions there was no loss of gold.

Owing to the seemingly contradictory information available an investigation was undertaken of the losses of gold during evaporation of various aqueous gold solutions.

EXPERIMENTAL

Gold-195 ($t_{1/2}$ 180 days) was produced by cyclotron irradiation of a 1-cm^2 platinum foil with 25 MeV protons for approximately 2 hr. The foil was dissolved in *aqua regia* and the nitrogen oxides were expelled by heating to dryness several times in the presence of small amounts of concentrated hydrochloric acid. The residue was dissolved in 3*M* hydrochloric acid containing 2 drops of phosphoric

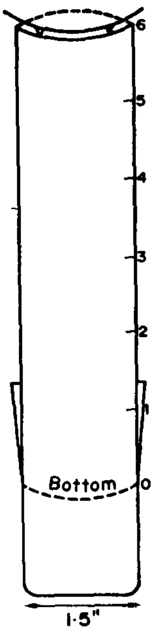


Fig. 1.—Evaporation beaker and chimney.

TABLE I.—DISTRIBUTION OF ^{195}Au AFTER SOLUTION EVAPORATION.

Activity of gold taken, *cps*	Solution	Temperature, °*C*	Activity, in chimney after evaporation, *cps*				
			Bottom	Side			
				0″	2″	4″	6″
1477	10 ml HCl (conc.)	78	1·4	1·3	0	0	0
1478	20 ml HCl (conc.)	78	15·8	7·8	7·6	0	0
1476	30 ml HCl (conc.)	78	15·5	9·8	9·1	2·5	0
1051	10 ml HCl (conc.)	90	6·3	2·6	2·2	0	0
1041	20 ml HCl (conc.)	90	8·7	7·5	6·4	0·6	0
1061	20 ml 6*M* HCl	90	24·2	12·4	12·1	0·8	0
1216	20 ml 1*M* HCl	90	8·1	5·7	3·3	0	0
3903	20 ml 6*M* HCl	78	6·7	5·9	5·3	2·8	1·2
315·5	0·5% NaCl + 20 ml 6*M* HCl	78	4·1	2·5	1·3	1·0	0·5
345·8	1·0% NaCl + 20 ml 6*M* HCl	78	3·8	1·8	0·8	0·7	0·1
457·0	4·5% NaCl + 20 ml 6*M* HCl	78	1·0	1·0	1·0	0	0
603·0	0·5% $CuCl_2$ + 20 ml 6*M* HCl	78	2·3	0·8	2·4	0·5	0
580·5	1·0% $CuCl_2$ + 20 ml 6*M* HCl	78	1·3	1·0	0·8	0	0
551·0	4·5% $CuCl_2$ + 20 ml 6*M* HCl	78	0·5	0·5	0	0	0
118·1	0·5% KCl + 20 ml 6*M* HCl	78	0·8	0·5	0	0	0
158·3	1·0% KCl + 20 ml 6*M* HCl	78	1·3	1·1	1·3	0	0
118·5	4·5% KCl + 20 ml 6*M* HCl	78	3·0	2·0	1·8	—	—
208·5	0·5% $FeCl_3$ + 20 ml 6*M* HCl	78	13·0	6·4	3·6	1·5	0·5
233·5	1·0% $FeCl_3$ + 20 ml 6*M* HCl	78	0·7	3·3	2·2	0·9	0·4
264·3	4·5% $FeCl_3$ + 20 ml 6*M* HCl	78	2·3	1·8	2·8	0	0
1475	1 mg $AuCl_3$ + 10 ml HCl (conc.)	78	0	0	0	0	0
1478	2 mg $AuCl_3$ + 20 ml 6*M* HCl	78	0	0	0	0	0
4735	1 μg $AuCl_3$ + 20 ml 6*M* HCl	78	3·5	1·8	2·8	1·0	0·8
5243	11 μg $AuCl_3$ + 20 ml 6*M* HCl	78	34·1	22·4	11·7	0·5	0·6
5179	111 μg $AuCl_3$ + 20 ml 6*M* HCl	78	4·2	4·6	4·0	1·7	0
1282	111 μg $AuCl_3$ + 20 ml H_2O	90	4·7	2·9	2·2	0	0
1242	20 ml HNO_3 (conc.)	90	6·4	2·8	2·2	0·8	0
1981	20 ml 7·8*M* HNO_3	90	6·6	3·8	4·7	0·5	0
891	20 ml 1·0*M* HNO_3	90	10·5	5·0	5·0	0	0
681	20 ml *aqua regia*	90	11·8	5·0	2·7	0	0
731	20 ml H_2SO_4 (conc.)	125	34·1	13·1	12·7	0	0
783	20 ml 8·9*M* H_2SO_4	125	6·7	3·8	2·5	0	0
941	20 ml 1·0*M* H_2SO_4	125	11·8	4·8	2·6	0	0
1317	50% ethanol:50% 6*M* HCl	78	5·2	2·8	2·4	0	0
1897	20 ml 6*M* HCl + 2 drops "Triton-X"	78	2·4	4·2	0	0	0
1442	20 ml 6*M* HCl + 1·0% agar agar	78	0·3	3·5	0·4	0	0
1623	20 ml 6*M* HCl + 0·5% agar agar	78	0	0	0	0	0
2213	20 ml 6*M* HCl + 2·5% agar agar	78	0	0	0	0	0
3858	20 ml 6*M* HCl*	78	1·7	0·7	0	0	0
3809	11 μg $AuCl_3$ + HCl (conc.)*	78	1·4	0·6	0·8	0	0
483	20 ml 6*M* HCl*	78	0	0	0	0	0
1304	20 ml 6*M* HCl†	78	0				
2537	20 ml 6*M* HCl†	78	0				

* Chimney separated from beaker by 2 mm, as a capillary action check.

† Cooling coil used directly above beaker but not in contact.

acid and the solution was extracted several times with equal volumes of ethyl acetate. The combined extracts were evaporated to dryness, decomposed with nitric acid and hydrogen peroxide, and then evaporated to dryness several times in the presence of concentrated hydrochloric acid. The auric chloride thus obtained was dissolved and made up to 10 ml with $2M$ hydrochloric acid. The radiopurity of the stock solution was confirmed by γ-spectrometry.

Special beakers were made from 34/35 ground-glass joints (Fig. 1) for the experiment.

Samples were prepared containing 1 ml of ^{195}Au solution. The conditions were varied by adding various volumes and strengths of acids, salts, inhibitors, desurfactants and non-radioactive gold, as shown in Table I. The beaker and chimney were assembled and put on a steam-bath, and the temperature noted. In some cases a water-bath or a hot-plate was used. After evaporation to dryness, the activity at the base of the chimney and the activity at different heights in the chimney were recorded as in Table I. Counting errors amount to approximately 2 cps. Any activity on the chimney was washed down into the beaker with the acid required for the next experiment and the chimney checked for residual activity.

As a check for capillary action, some experiments were run with the chimney separated from the beaker by 2 mm, and the solutions were evaporated to dryness. Several solutions were also evaporated to dryness with a cooling coil placed just above but not in contact with the beaker. As shown by the results in Table I, there was no appreciable activity on the cooling coil or chimney.

Some of the experiments which showed a significant migration of gold were repeated with various concentrations of inhibitors such as agar agar or salts or substances such as "Triton-X" or ethanol.

DISCUSSION

The results indicate that gold does not volatilize appreciably from aqueous solutions but that it does have a significant ability to creep. The use of salts, non-radioactive gold and agar agar significantly suppresses the creeping of gold solutions, whereas the use of more volatile solvents does not seem to have any significant effect. When concentrated acids are used the degree of creeping seems directly related to the viscosity of the acid. The absence of significant activity on the separated chimney and the absence of gold on the cooling coil show that gold is not volatile under the various conditions used. The results also indicate that while losses as high as 2 or 3% may occur *via* creeping when submicrogram amounts of gold are used, the presence of even microgram amounts of gold is sufficient to suppress the loss significantly.

Thus because of creeping, it is necessary to use particular care in washing the beaker walls to ensure that a quantitative recovery of gold is obtained after any procedure involving the evaporation of a solution containing gold. The losses formerly attributed by some authors to volatilization were probably due to difficulties caused by creeping.

Acknowledgement—The authors wish to thank the National Research Council of Canada for its financial support and Johnson Matthey and Mallory Ltd. (Toronto, Canada) for providing the gold used.

Department of Chemistry
University of Manitoba
Winnipeg, Canada

D. Buksak
A. Chow

Summary—The study indicates that despite several reports to the contrary, gold does not volatilize appreciably during the evaporation of aqueous solutions. Gold solutions were shown to have a tendency to creep significantly in solutions of various metal concentrations, acid content and salt content, and that careful washing must be carried out to obtain quantitative recovery.

Zusammenfassung—Die Untersuchung zeigt, daß entgegen mehreren Angaben Gold während des Eindampfens wäßriger Lösungen nicht merklich flüchtig geht. Es wird gezeigt, daß Goldlösungen in verschiedenen Metallkonzentrationen, Säure- und Salzgehalten beträchtlich zum Kriechen neigen und daß daher sorgfältig gewaschen werden muß, um quantitative Ergebnisse zu erhalten.

Résumé—L'étude indique que, malgré plusieurs indications contraires, l'or ne se volatilise pas de manière appréciable durant l'évaporation de solutions aqueuses. On a montré que les solutions d'or ont une tendance à "grimper" de manière importante dans des solutions de concentrations en métal, teneur en acide et teneur en sel diverses, et qu'il convient de procéder à un lavage soigné pour obtenir une récupération quantitative.

REFERENCES

1. A. Mizuike and Y. Takata, *Bunseki Kagaku*, 1963, **12**, 1192.
2. R. Gilchrist, *J. Res. Natl. Bur. Stds.*, 1938, **20**, 747.
3. I. N. Plaksin and M. A. Koyukhova, *Tsvetn. Metal.*, 1931, **6**, 35.
4. H. V. Weiss and Ming-Gon Lai, *Anal. Chim. Acta*, 1963, **28**, 242.
5. C. B. Brodigan, *Met. Chem. Eng.*, **12**, 460.
6. M. Gachev, *Minno Delo Met. Sofia*, 1963, **18**, (12), 35.
7. E. I. Novikova, *Sb. Nauchn. Tr. Kazakhsk. Gorno-Met. Inst.*, 1959, **20**, 399.
8. F. W. Chapman, Jr., G. G. Marvin and S. Y. Tyree, Jr., *Anal. Chem.*, 1949, **21**, 700.

Talanta, 1972, Vol. 19, pp. 1486 to 1487. Pergamon Press. Printed in Northern Ireland

Modifications of the computer programme SCOGS

(*Received* 13 *December* 1971. *Accepted* 20 *January* 1972)

THE COMPUTER PROGRAMME SCOGS[1,2] was developed to extract "best-fit" equilibrium constants for acid dissociation or metal-complex formation from pH-titration data. On the basis of some experience in the use of this programme we offer the following comments and modifications.

The programme is designed to generate or utilize "mixed" acidity constants of the type $K_a = H[A]/[HA]$, where $H = 10^{-pH}$. Similarly, expressions for formation constants of protonated metal complexes contain H, and those of deprotonated species, including products of hydrolysis of metallic ions, contain $OH = 10^{pH-pK_w}$. Many workers, including the authors, prefer to express these quantities as concentration quotients, and we have accordingly modified the computer programme for this purpose. To do so we required some rationale for converting pH value into hydrogen-ion concentrations. In the original description of SCOGS this was accomplished by means of an appropriate value for the activity coefficient of hydrogen ion; this appears to have been a suitable mean activity coefficient $f_{\pm}$. Subsequent users of the programme[3] introduced the notion that, since this conversion factor ($F = H/[H]$) could not strictly be evaluated on theoretical grounds, it be treated as an adjustable parameter within the computer programme. The most suitable value of F was that leading to minimum standard deviation in titre (SDT). Alternatively, F can be directly evaluated with solutions of known hydrogen-ion concentration,[4-6] and this is the authors' practice.

It is also advantageous to express K_w as a concentration quotient, K_{cw}. Where appropriate data are available the value of K_{cw} can be estimated from values of K_w and the factor $\gamma_H\gamma_{OH}/a_{H_2O}$.[7] Where such data are lacking, K_{cw} can be found by suitably combining the results of pH measurements in acid and alkaline solutions of known composition.[6]

The changes required in the original SCOGS programme then become:

(1) Main programme, card 0094
  —use value of ionic concentration product
  —use value of F appropriate to the solvent medium
(2) Main programme, card 0105
  —from 129 UXS (K) = 10**U(K)
  —to 129 UXS(K) = 10**U(K)*F
(3) Subroutine COGSNR, card 0039
  —from HO = HO/F
  —to DELETE THIS CARD

The extensive capabilities of SCOGS are achieved at the expense of a fair amount of computer time. The authors have found that savings in central processing-unit time of about 30–40% can be achieved by the use of the FORTRAN H compiler (rather than FORTRAN G). Further saving in compiling time is achieved by having the programme produced as an object deck, or alternatively by storing the object module on a direct access tape or drum. The authors would be pleased to supply a listing of the modified programme on request.

The original description of the programme fails to make clear that formation constants for any deprotonated species are incorporated or produced in the form appropriate to a proton-releasing

REFERENCES

1. A. Mizuike and Y. Takata, *Bunseki Kagaku*, 1963, **12**, 1192.
2. R. Gilchrist, *J. Res. Natl. Bur. Stds.*, 1938, **20**, 747.
3. I. N. Plaksin and M. A. Koyukhova, *Tsvetn. Metal.*, 1931, **6**, 35.
4. H. V. Weiss and Ming-Gon Lai, *Anal. Chim. Acta*, 1963, **28**, 242.
5. C. B. Brodigan, *Met. Chem. Eng.*, **12**, 460.
6. M. Gachev, *Minno Delo Met. Sofia*, 1963, **18**, (12), 35.
7. E. I. Novikova, *Sb. Nauchn. Tr. Kazakhsk. Gorno-Met. Inst.*, 1959, **20**, 399.
8. F. W. Chapman, Jr., G. G. Marvin and S. Y. Tyree, Jr., *Anal. Chem.*, 1949, **21**, 700.

Talanta, 1972, Vol. 19, pp. 1486 to 1487. Pergamon Press. Printed in Northern Ireland

Modifications of the computer programme SCOGS

(*Received* 13 *December* 1971. *Accepted* 20 *January* 1972)

THE COMPUTER PROGRAMME SCOGS[1,2] was developed to extract "best-fit" equilibrium constants for acid dissociation or metal-complex formation from pH-titration data. On the basis of some experience in the use of this programme we offer the following comments and modifications.

The programme is designed to generate or utilize "mixed" acidity constants of the type $K_a = \mathrm{H[A]/[HA]}$, where $\mathrm{H} = 10^{-\mathrm{pH}}$. Similarly, expressions for formation constants of protonated metal complexes contain H, and those of deprotonated species, including products of hydrolysis of metallic ions, contain $\mathrm{OH} = 10^{\mathrm{pH}-\mathrm{p}K_w}$. Many workers, including the authors, prefer to express these quantities as concentration quotients, and we have accordingly modified the computer programme for this purpose. To do so we required some rationale for converting pH value into hydrogen-ion concentrations. In the original description of SCOGS this was accomplished by means of an appropriate value for the activity coefficient of hydrogen ion; this appears to have been a suitable mean activity coefficient $f_{\pm}$. Subsequent users of the programme[3] introduced the notion that, since this conversion factor (F = H/[H]) could not strictly be evaluated on theoretical grounds, it be treated as an adjustable parameter within the computer programme. The most suitable value of F was that leading to minimum standard deviation in titre (SDT). Alternatively, F can be directly evaluated with solutions of known hydrogen-ion concentration,[4-6] and this is the authors' practice.

It is also advantageous to express K_w as a concentration quotient, K_{cw}. Where appropriate data are available the value of K_{cw} can be estimated from values of K_w and the factor $\gamma_H\gamma_{OH}/a_{H_2O}$.[7] Where such data are lacking, K_{cw} can be found by suitably combining the results of pH measurements in acid and alkaline solutions of known composition.[6]

The changes required in the original SCOGS programme then become:

(1) Main programme, card 0094
 —use value of ionic concentration product
 —use value of F appropriate to the solvent medium
(2) Main programme, card 0105
 —from 129 UXS (K) = 10**U(K)
 —to 129 UXS(K) = 10**U(K)*F
(3) Subroutine COGSNR, card 0039
 —from HO = HO/F
 —to DELETE THIS CARD

The extensive capabilities of SCOGS are achieved at the expense of a fair amount of computer time. The authors have found that savings in central processing-unit time of about 30–40% can be achieved by the use of the FORTRAN H compiler (rather than FORTRAN G). Further saving in compiling time is achieved by having the programme produced as an object deck, or alternatively by storing the object module on a direct access tape or drum. The authors would be pleased to supply a listing of the modified programme on request.

The original description of the programme fails to make clear that formation constants for any deprotonated species are incorporated or produced in the form appropriate to a proton-releasing reaction, *e.g.*,

$$M + H_2O = MOH + H$$
$$M + L + H_2O = MOHL + H, \textit{etc.}$$

There is also a contradiction in the published account[1] concerning the significance of the residual R_i. The statement on p. 1398 is at variance with the instruction on card 0161 of the main programme; the residual is, in fact, the calculated titre minus the actual titre. Since modification or introduction of new trial equilibrium constants as input data is often based on interpretation of the significance of individual residuals, it is important that the sign of each residual be correctly understood.

Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada

W. A. E. McBryde
J. L. McCourt

Summary—The computer programme SCOGS has been modified to accept and yield all equilibrium constants involving proton transfer, as concentration quotients. Significant savings in operating time are achieved through use of the FORTRAN H compiler.

Zusammenfassung—Das Rechnerprogramm SCOGS wurde abgeändert, um alle Gleichgewichtskonstanten aufzunehmen oder zu liefern, die mit Protonenübergängen zu tun haben, und zwar in der Form von Konzentrationsverhältnissen. Beträchtliche Einsparungen an Bedienungszeit werden durch Verwendung des FORTRAN H-Kompilierers erzielt.

Résumé—On a modifié le programme de calculatrice SCOGS pour accepter et rendre toutes les constantes d'équilibre impliquées dans le transfert de proton, comme les quotients de concentration. Des économies importantes dans le temps d'opération peuvent être réalisées par l'emploi du compilateur FORTRAN H.

REFERENCES

1. I. G. Sayce, *Talanta*, 1968, **15**, 1397.
2. *Idem, ibid.*, 1970, **18**, 653.
3. C. W. Childs and D. D. Perrin, *J. Chem. Soc. A*, 1969, 1039.
4. H. M. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475.
5. W. A. E. McBryde, *Analyst*, 1969, **94**, 337.
6. *Idem, ibid.*, 1971, **96**, 739.
7. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions*, 3rd Ed., pp. 752–4, Reinhold, New York, 1958.

Talanta, 1972, Vol. 19, pp. 1489 to 1521. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

EXTREME TRACE ANALYSIS OF THE ELEMENTS—I

METHODS AND PROBLEMS OF SAMPLE TREATMENT, SEPARATION AND ENRICHMENT

GÜNTHER TÖLG
Max-Planck-Institut für Metallforschung, Laboratorium für Reinststoffe,
7070-Schwäbisch Gmünd, Katharinenstraße 17, B.R.D.

(*Received* 5 *May* 1971. *Accepted* 17 *March* 1972)

Summary—In the determination of elements in the ppM range in inorganic and organic matrices, solution techniques are useful because they simplify calibration problems and improve the limit of detection. The author reviews, in the light of his own experience, some 350 publications concerned with methods for the preparation and dissolution of samples and for the isolation of trace elements before their determination. The errors in these methods, made more difficult to reduce because of the additional operations required, are compared with those associated with the more direct methods.

WHILE micro- and ultramicro elemental analysis[1,2] is concerned with the determination of major and minor constituents ($10^{-2}\%$) in small samples (<10 mg), the aim of trace analysis[3–19] is to detect the elements in an amount of matrix material at least 10^4 times as great, *i.e.* at the ppm or ppM level. Thus in microanalysis the small amount to be determined is dictated by the small amount of sample available, but in trace analysis by its very low concentration in the matrix.

Confusion has arisen through the unfortunately frequent inconsistent usage of the terms "micro-" and "trace-", particularly in connection with literature documentation. For this reason one ought to characterize the techniques of trace analysis according to the concentrations which can be handled, in the same way that those of microanalysis are classified according to size of sample.[21–22] Thus instead of "trace analytical techniques" we should say ppm-techniques (1 ppm $= 10^{-4}\%$), and instead of "ultra- or micro-trace techniques" ppM-techniques (1 ppM $= 10^{-7}\%$). The former are nowadays in routine use; this review is to deal with the ppM-techniques and also ppm-techniques applied to samples of limited size—so-called ppm-microtechniques. The absolute amounts of the elements which can be determined by methods presently at our disposal lie in both cases in the ng and upper pg ranges, and in a few cases even lower.

The extremely low limits of detection required for methods that are to cope with such small amounts (Table I) are often raised by several orders of magnitude, depending on the matrix and the trace element, by the high concentration of the matrix element. For this reason one can rarely avoid the necessity of separating or at least concentrating the trace elements sought in cases of extreme trace analysis. In addition to the specialized vaporization procedures involving direct excitation of the sample

---

* For reprints of this Review see Publisher's announcement near end of this issue.

TABLE I.—METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF ELEMENTS

Method	Limit of detection,* g	Remarks
Titrimetric methods	10^{-9}	electrometric indication
Spectrophotometry	10^{-10}	capillary cells
Fluorimetry	10^{-11}	capillary cells
X-ray fluorescence	10^{-9}	bowed crystals
Electron-probe microanalysis	10^{-14}	calculated
Polarographic methods	10^{-10}	stripping methods
Gas chromatography	10^{-12}	ECD or FID
Atomic-absorption spectroscopy	10^{-13}	non-flame technique
Emission spectroscopy	10^{-10}	solution methods
Catalytic methods	10^{-12}	
Isotope-dilution and radiochemical methods	10^{-12}	substoichiometric extraction
Neutron-activation analysis	10^{-14}†	large cross-sections, short half-lives
Mass spectroscopy	10^{-16}	calculated

* Favourable limit of detection for a particularly easily determined element. These can only be very approximate estimates for reasonably favourable conditions, and may be very readily influenced by many experimental factors.

† For neutron flux of 10^{14} neutrons/cm^2/sec.

in spectroscopic analysis, there are procedures with good limits of detection (10^{-9}–10^{-14} g) which can be applied to the analysis of small volumes of more concentrated solutions. Some techniques well suited to this approach include solution spectroscopy,[23–30] inverse voltammetry,[31,32] and gas chromatography.[33,345] Traces, enriched on the surface of a very small target, can also be excited by laser-, electron-, or ion-beam irradiation for spectrographic analysis.

The increased expense and the propagation of errors occasioned by the additional manipulation and handling steps in the preconcentration procedures have to be accepted. The separation problems are frequently very difficult, being made even more so by the variety of matrices which may be encountered.

The matrix is sometimes a single element, as in the analysis of high-purity materials such as metals,[16,18,34] semiconductors,[7,13,16,35] and reactor materials,[36–38] but more often is a combination of elements (compounds, mixtures, alloys, *etc*) as in the case of geological[39] and lunar[41] samples and organic and biological materials.[17,20,39] Foodstuffs,[40] water,[41–43] and air[44–48] are increasing in importance as matrices with the mounting concern about the environment.

We regrettably know little about the causes of the numerous predominant systematic errors in extreme trace analysis. The literature gives only rough generalized rules for reducing them, and it cannot be too strongly emphasized that these rules must not be used uncritically, since chemically similar species can show marked differences of behaviour under similar conditions. For this reason, each individual step of a procedure under development for extreme trace analysis—the preparation, weighing, dissolution, separation or concentration of the trace element—must be carefully investigated for sources of error and their causes.

This, the first of two parts of a review article, will go into the problems met with in extreme trace analysis in the processes of dissolution, separation and preconcentration.

RELIABILITY, DETECTION CRITERIA AND CALIBRATION

The reliability of a trace analytical method is characterized by its "reproducibility", depending on statistical errors and precision, and its accuracy, depending on systematic errors. Both terms have been clearly defined in the literature.[49–51] In the case of microanalytical techniques for the determination of major or minor components in small samples, reproducibility is of great importance; systematic errors can be relatively easily avoided when working with concentrations $>10^{-3}M$. In trace analysis good reproducibility is of course desirable, but a lower accuracy of determination of lower concentrations must be accepted. Thus for example trace element concentrations in biological and geological materials are in any case subject to enormous variation,[52] or again, the quantity to be determined may be only just above the limit of detection for the particular method (see next section). Great attention must be given to avoiding systematic errors in trace analysis methods which involve dissolution and separation. The problem of calibration must be considered carefully, in particular when dealing with ppM techniques.

Statistical errors, limits of detection and determination

With all instrumental techniques, even in the supposed absence of the element to be determined there is a statistical variation of the analytical signal—the so-called noise-level, or blank value. This can be caused by variations in operating conditions of sources or detectors (*e.g.*, noise in the electronics, voltage fluctuations) or by impurities being carried into the excitation cell. When various procedures are combined in a method—weighing, dissolution, preconcentration, and determination—the individual blank values are combined according to the law of propagation of errors.[53] The amount of an element to be determined must therefore be greater than the total blank value and its variation.

Kaiser suggested[53–55] that a signal (X) could be considered with reasonable confidence to be different from the blank value when it is at least as great as the mean blank value $\bar{X}_{\mathrm{b}(N)}$ plus three standard deviations of the blank value ($s_{\bar{X}_{\mathrm{b}(N)}}$):

$$X = \bar{X}_{\mathrm{b}(N)} + 3s_{\bar{X}_{\mathrm{b}(N)}}$$

The limit of detection thus determined can be given with greater confidence if a larger number (N) of determinations of the blank value $\bar{X}_{\mathrm{b}(N)}$ is made. At least 20 measurements of the blank value should be used.[54]

According to this criterion the smallest amount of the element which might be detected, is done so with a probability of only 0·5. Feigl[56] preferred to define a limit of determination—which has been discussed at some length[18]—which implies, for homogeneous samples, Kaiser's "limits for the guarantee of purity":[54]

$$X = \bar{X}_{\mathrm{b}(N)} + 6s_{\bar{X}_{\mathrm{b}(N)}}$$

Ehrlich has indicated the difference between the two concepts when applied to inhomogeneous samples.[18]

The relative standard deviation for an analytical procedure in the vicinity of the limit of determination is $\geqslant 33\%$.[53] Mathematically speaking, the sensitivity of a method can even better be applied as a guarantee of the highest possible purity.[18] Püschel describes a linear relationship between the concentration of the determinand

and the reproducibility over the range 10^{-4}–100%. This proportionality remains to be tested for lower concentrations.

Systematic errors[58]

Even if reproducible blank values and small statistical errors are inherent in a method, the analytical results may deviate in either direction from the true values. This may be the case, for example, when the standardization and the analysis are not carried out in exactly the same manner. It is, however, very difficult to work out such comprehensive instructions for a trace analysis procedure, since the sources of error vary from one sample to the next and cannot always be anticipated. The relevance of systematic errors is best illustrated by an example.

In the spectrophotometric determination of selenium in effluents (selenium concentration $\leqslant 0{\cdot}02$ ppm) traces of selenium can be lost by irreversible adsorption on the surface of the container even during very short storage periods. The degree of adsorption is dependent on the nature of the surface material, its pretreatment, the pH of the solution, the contact time, and a number of other parameters. Another portion of the selenium can be lost by evaporation during boiling down of the aqueous sample or mineralization of the residue, or can again be lost by adsorption. Loss of selenium can also occur during separation from interfering elements, or the chromophoric reagent may have undergone some change during the time between the calibration and the analysis. Values that are too high can be encountered when glassware contaminated with selenium is used, or when the selenium content of a reagent has increased.

Püschel's relationship between concentration and reproducibility for levels above 1 ppm does not hold with any certainty for lower concentrations. The difficulty of eliminating systematic errors becomes increasingly greater with decreasing levels in the ppM region, and eventually the principal problem.

In extreme trace analysis, standard samples are simply not available, and for this reason it is no longer possible to compensate for systematic errors by calibration. Other ways must be found, as follows.

(1) A carefully chosen sample is investigated by at least two or three different methods involving different sources of systematic error. However, even if enough different procedures are available, and each has good reproducibility, no agreement may be found between the results.

(2) Varying amounts of the same sample are analysed or varying amounts of standard solution of the determinand are added to a constant amount of sample before analysis. The results are plotted against sample weight or concentration added, and only when the curve can be extrapolated through the origin, is systematic error absent. Even so, for the extrapolated region itself, nothing can be said about the systematic errors. It is also possible that the added element is present in a different oxidation state or in a more reactive compound than it is in the sample, and thus behaves differently.

(3) If the element to be determined has a radioactive isotope with convenient half-life and decay pattern, then the systematic errors can be reduced by using isotope dilution analysis.[59–66] A small amount of the radioactive isotope is added to the sample before the analysis, and the activity is followed till the end of the procedure. The result is then corrected according to the radiochemically determined yield.

(4) By far the best solution lies in optimizing the procedure so that the systematic errors are reduced to a minimum. Comprehensive statistically significant yield determinations are rather laborious, but always worthwhile. Whenever possible, radiochemical tracer methods[59,61–63,65] should be used. In applied extreme trace analysis the goal is generally reached by a combination of routes.

Calibration problems

The majority of direct instrumental methods of trace analysis are matrix-dependent, and rely on comparison with analysed standards. But if the concentration levels are very low, reliably analysed samples of similar composition to that of the unknown are generally not available. Only in a few cases can high-purity materials such as water, gases, mercury, aluminium, germanium and arsenic be doped to make suitable standards and even then the homogeneity of the product is always open to doubt. Standard addition procedures and the use of internal standards have their limitations, as already mentioned. A further possibility is to calibrate by using very small samples, weighed on an ultramicrobalance, of accurately analysed standards with relatively high contents of the element sought. By using such a procedure it is possible to calibrate a method for the determination of carbon in high-purity iron, with ordinary steel samples as standards.

In contrast, methods of determination combined with separation techniques are much easier to calibrate. Standard solutions around 10^{-3}–$10^{-4}M$ and prepared from high-purity materials, may be handled with ultramicro pipettes or burettes[1] readable to 0·01 μl, allowing most solution techniques such as emission spectrography, atomic-absorption spectroscopy and inverse voltammetry to be calibrated for many elements even in the picogram range, in some cases with statistical errors $<2\%$. In this way separation and determination methods can compete in many cases with direct determination methods of high sensitivity such as neutron activation analysis and solid-source mass spectrometry.

SOURCES OF ERROR AND MINIMIZATION OF ERRORS

As a general rule the blank value (impurities introduced by reagents, apparatus and laboratory air) primarily affects the reproducibility and limit of detection of an analysis while adsorption and volatilization tend to affect the accuracy. The order of magnitude of the individual errors varies greatly from element to element, and from one dissolution and separation procedure to another, so that the following considerations can only be considered as generalizations.

The laboratory

Special standards of cleanliness must be adhered to in laboratories where extreme trace analysis is to be carried out.[10–12,14,16,18,19,67] In addition to the particularly common elements in air, such as Si, Al, Fe, Ca, Na, K, Mg, C, Ti, Cl, P and S, the atmosphere in densely populated areas also contains less common elements including Pb, V, Zn, Ni, Cr, Cu, Br and F at concentrations above 0·1 μg/m^3.[68,69] In laboratory air these and other elements such as mercury may be present at much higher levels. The dust in laboratories contains many unusual elements at low levels, depending on the type of work normally being carried out. Thus Ag, Au, Ga, In, Tl, Bi, As, Sb have all been found in relatively high concentrations.[14] The sources of all these impurities, which should be sought both outside and inside the laboratory, include building and industrial dust, rust, exhaust fumes and gases from motor vehicles and factories, as well as natural materials such as pollens. Thus microparticles of the most diverse compositions may be derived from wear on floors, walls and ceilings, from clothing and from the skin of persons working in the laboratory. Air-dried healthy skin has been shown to contain typically about 6 ppm Zn, 0·7 ppm Cu, 0·03 ppm Ag, 0·77 ppm As and 0·002 ppm Au.[70] Traces of silver and gold may be derived from articles of jewellery, and traces of zinc from cosmetics.

Corroding constructional materials considerably increase the levels of Fe, Cr, Ni, and Mo, and increased levels of Cu and Zn may be traced in many cases to heating equipment such as water-heaters, steam-baths, sand-baths and gas burners. The evaporation of solvents from floor polishes can add to the C and P levels of the atmosphere, and also cause periodic variations in these levels. Gas flames contaminate the air heavily with S; detergents and cleaning materials introduce Na, Mg, B, P, C, S *etc.*[1]

The use of plastic glove-boxes which can be flushed with purified air or an inert gas, helps to reduce all sources of contamination very considerably.[14,16,18,71] Special arrangements have also been described[71] for working with a dry atmosphere. Instead of work in the open laboratory for the dissolution of samples or evaporation of solutions, completely sealed vessels are used,[1,6,72,73] or the whole analytical procedure takes place in a closed, programmed system in which the sample is protected from contamination from the air at all stages except the first one of transfer to the system.

Nowadays, however, even more stringent purity conditions can be achieved. The development of high-capacity air filters has progressed so far in recent years that whole rooms may now be maintained substantially free from dust and suspended particles.[74,75] Such "clean rooms" are flushed with a laminar flow of clean air, either horizontally or vertically, and may only be entered through air-locks, with specially dust-free protective clothing being worn. There are three standards of cleanliness.[75] In class I rooms—those with the highest standard—there should be, per cubic metre, fewer than $3{\cdot}5 \times 10^3$ particles with size above 0·5 μm, and none greater than 5 μm. When planning our own laboratories for the analysis of high-purity materials, we adopted a slightly less stringent but nevertheless very effective approach. In clean rooms of class III (non-laminar flow; $3{\cdot}5 \times 10^6/\text{m}^3$ and $25 \times 10^3/\text{m}^3$ for 0·5–5 μm and 5 μm particles respectively) "clean benches"[76] have been set up. They have the dimensions of normal fume-cupboards in chemical laboratories, and are flushed with filtered air according to the laminar-flow principle (Fig. 1) in such a way that chemical vapours can be sucked outside the clean area altogether. This concept permits all chemical stages of sample preparation, up to introduction of the sample into the instrument, to be done on the "clean benches", and also the instruments such as spectrographs, gas chromatographs, *etc*, to be kept in a state of highest cleanliness, and with full air-conditioning. For work in a metal-free environment the inside of the "clean bench" should be completely lined with polypropylene.

The residual dust-particle count in a clean-room, and the particle-size distribution must be continuously monitored by light-scattering measurements in order to detect leaks or sources of turbulence in good time. The rooms should be laid out and equipped so that at least 25 m^2 are allowed per person working there. The sole source of heat in these rooms should be electrical elements sealed into quartz.

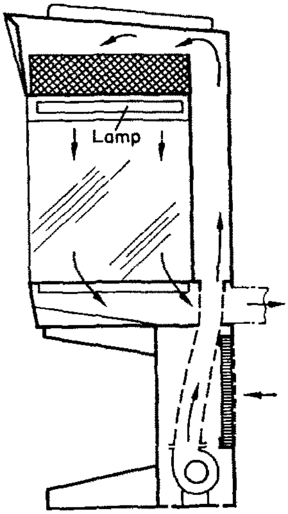


FIG. 1.—Cross-section of a "clean bench" working on the principle of laminar flow downwards displacement. (South London Electrical Equipment Co. Ltd., London, S.E. 13)

By working with a "clean bench" instead of a glove-box in the determination of silicon in high-purity materials, it has been possible to reduce by a factor of more than ten, the blank value due to contamination from laboratory air.[77]

Exchange processes between solutions and vessels

Even highly polished glass and quartz surfaces possess a much higher active surface area than their apparent geometrical surface area would suggest, since they still possess quite a marked surface structure, in terms of irregularities of the order of 0·1 μm depth or less. This results in pronounced adsorption and desorption exchange reactions taking place between the surface and the solution. As a rule, such effects first become noticeable at concentrations below $10^{-3}M$, as slow time-dependent changes in concentration. In very dilute solutions, however, the decrease in concentration can be quite rapid. On the other hand high purity acids, alkalis, and solutions of complexing agents tend to dissolve impurities out of the surface (see below) and both effects could be operative.

Adsorption. Very few measurements on adsorption of ions from aqueous solutions on to surfaces in common use for trace analysis can be usefully compared, since a multitude of parameters such as container material, nature of the ions, concentrations, pH values, other ions present, contact time, and, not least, the manufacture and pretreatment of the surface all complicate the investigations. In addition, the processes of ion-exchange must be considered.[78] The losses would seem to amount to something of the order of 10^{-9}–10^{-12} mole/cm^2. In many cases the effects decrease for the sequence of materials borosilicate glass, soda glass, platinum, silica, polythene, polypropylene, Teflon.[79–83] But there are many exceptions. For example, Ce^{3+}, Be^{2+} and La^{3+} are more weakly adsorbed onto glass than onto polypropylene from aqueous solutions,[84] and the same has been shown to hold for phosphate.[85] For aqueous $^{60}Co(II)$ solutions ($2 \times 10^{-5}M$) increasing adsorption was found, in the sequence silica, Teflon, polythene, glass, at pH 9, but at pH 1·5 silica adsorbed more strongly

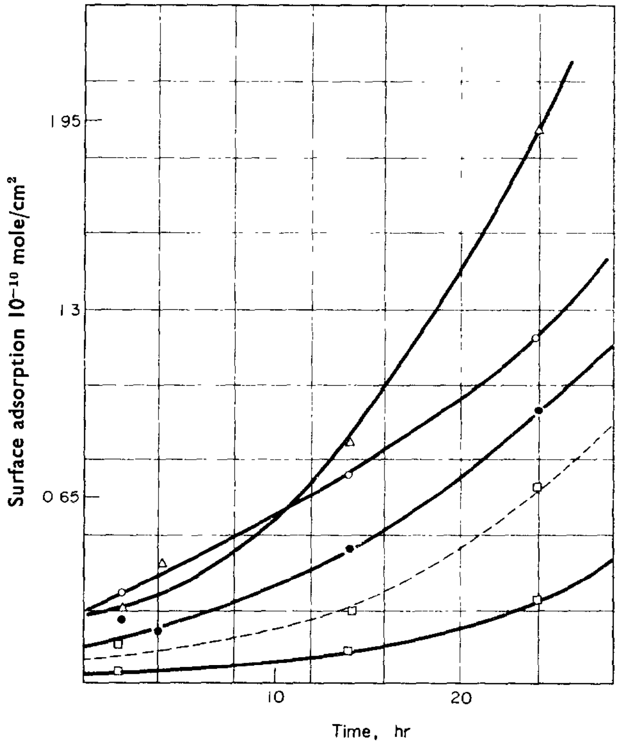


FIG. 2.—Adsorption of ^{60}Co(II) ions on different materials at pH 9 as a function of time.

—△— Glass G20, polished
—□— fused silica
—○— polythene
- -□- - fused silica, grinded
—●— Teflon

than Teflon (Figs. 2 and 3). Studies with ^{65}Zn(II) at the same concentration and under the same conditions showed adsorption increasing in the sequence Teflon, polythene, silica, glass at pH 9, whereas at pH 1·5 silica adsorbed more weakly than polythene.[86]

The dependence of the adsorption on the nature of the ion may be gathered from the following examples: Pb^{2+} and H^+ are more strongly adsorbed on glass than are Cu^{2+}, Ba^{2+} and K^+.[87] Silver ions show a pronounced tendency to be adsorbed from aqueous solutions onto glass,[79] as do Th^{4+} ions from uranyl nitrate solution.[78] Zinc is adsorbed much less strongly than cobalt.[86] Long-term studies with the ions of Sc, Fe, Zn, Co, Pb, Ag, In, Sb, Cs, U and Sr in aqueous solutions have shown differences in their behaviour towards polythene and Pyrex glass.[88] A change in oxidation state of an ion also affects the adsorption properties.[89]

The adsorption of one ionic species can be strongly affected by the presence of another in the same solution; for example, the adsorption of aluminium on silica is strongly reduced in the presence of sodium chloride.[90] Generally speaking, metal ions are less strongly adsorbed from acid solutions than from alkaline or neutral ones. In the case of ^{60}Co(II) and ^{65}Zn(II) ions, adsorption increased markedly above pH 8 on Teflon and polythene, and even more so on glass. Depending on the contact time, the adsorption is 10–20 times as great at pH 9 as at pH 5.[86] Naturally the dependence

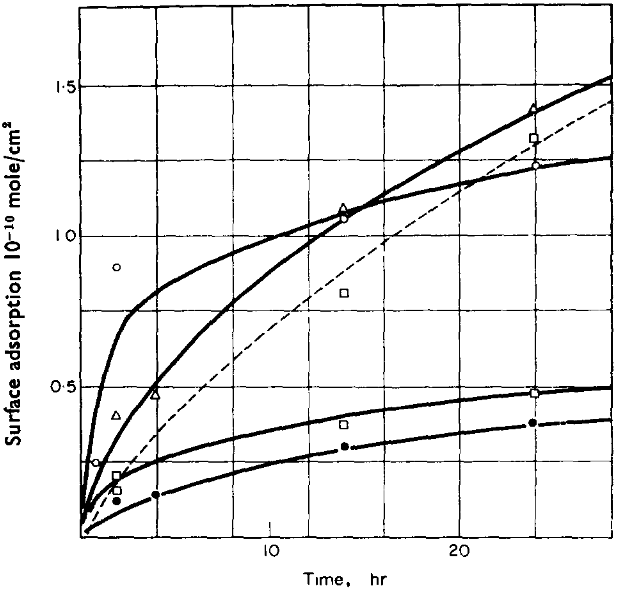


FIG. 3.—Adsorption of ^{60}Co(II) ions on different materials at pH 1·5, as a function of time.[86]
(same symbols as in Fig. 2.)

on pH is much greater in the case of glass or silica, and not only are there small variations, but completely different dependences, as exemplified by thorium adsorption glass and polythene.[89] Cations which tend to form colloids (*e.g.*, Tl^{3+}, UO_2^{2+}, Y^{3+}, Ru^{3+}) exhibit a maximum adsorption at a pH dependent on the isoelectric point.[19,20]

Reproducible adsorption of an ionic species presupposes that the surface remains the same, and hence the processing and pretreatment of the surface of the apparatus play an important role. Chromium is very strongly adsorbed onto glass surfaces from chromic acid: glassware to be used for trace analysis must therefore not be cleaned with this reagent. Treatment of glass surfaces with silicones brings about little improvement; the films are not resistant to alkali, and in any case tend to introduce other impurities into the system.[84]

For most purposes it is recommended that apparatus be degreased with acetone, and left standing for some time in acid. The particular effectiveness of the acid treatment is attributable to the strong bonding of hydrogen ions to glass surfaces.[87]

Comparative experiments using ^{60}Co(II) solutions and glass or silica surfaces showed that adsorption was reduced much more by soaking for one hour at room temperature in 2% hydrofluoric acid, or boiling out with 6*M* hydrochloric acid, or soaking for five hours in hot 2*M* sodium hydroxide, than by simple steam treatment. Minimum adsorption was found to occur after boiling with 6*M* hydrochloric acid.[86]

Most ionic species are retained by filter paper in amounts depending on the nature and concentration of the ion, the paper, and the pH, but varying between 10^{-4} and 10^{-7} g/cm². Adsorption on to pure asbestos, glass-wool, and cotton-wool is of the same magnitude.[19] Because of this, if at all possible filtration should be avoided in cases when the ions sought are those remaining in solution after a precipitation; An exception is the separation of elements by co-precipitation; here the important factor is interference from foreign ions introduced by the material of the filter (see below).

As our present knowledge of the adsorption behaviour of ionic solutions is so limited when compared to what we know about the materials used in trace analysis, the results just presented should in no case be generalized; in the investigation of any new separation procedure for trace quantities, studies on adsorption must be included. The adsorption of water and gases depends on more than just the humidity or the partial pressure, as the case may be, and the temperature; it is also strongly dependent on the nature of the material and the previous treatment of the surface. The amount of water adsorbed on glass[1]—depending on the type of glass—varies at room temperature between 0·3 and 20 $\mu g/cm^2$. Simple soda glasses,[91] silica and platinum show rather little adsorption, but in contrast, agate[92] can adsorb up to 160 $\mu g/cm^2$. Silicate-rich soda-lime glasses adsorb less than high-alkali ones. Artificial aging by steam treatment is said to diminish the adsorption of water.[92] This is an important source of error in the determination of trace amounts of water and oxygen in high-purity materials, and one which controls the limit of detection in all conventional methods for the determination of oxygen, if the oxygen content of the adsorbed water or the oxide film on the sample is of the same order of magnitude as that of the sample itself. In such cases it is only possible to obtain an accurate value by using the temperature gradient method[93] or activation analysis.[94,95]

Desorption. Since neither completely pure nor completely inert materials are known, great difficulties are encountered in the preparation, storage, and usage of not only corrosive acids, alkalis, and solutions of complexing agents but also high-purity water, without the introduction of contaminating residues from the materials of the containers. Errors in trace analysis, from these sources, are increased by long storage and use of high temperatures. Here only the question of storage of high-purity reagents will be discussed. Yet again our experience is severely limited, as the procedures used depend on the particular reagent being investigated, and the methods are very tedious.

For long-term storage of reagents only vessels of quartz, Teflon, and in some cases polythene or polypropylene[96] should be used. Results are available from long-term studies on these materials exposed to hydrofluoric, hydrochloric and nitric acids, and also to pure water.[16,97] Twenty-two elements were sought spectrographically. The levels of twelve were below the limits of detection (Bi, W, Ga, In, Au, Ag, Mo, Sn, Sb, Tl, Ta and Zn). The amounts of Al, Fe, Ca and Mg in the acids stored in Teflon and polythene vessels changed very little during the thirty days storage. Nitric and hydrochloric acids took only a very small amount of magnesium from silica. When high-purity water with Ca, Mg, Ti and Cu contents in the range 10^{7}–10^{-10}% was stored in Teflon or polythene for thirty days, these levels increased by factors between five and ten, and in addition small amounts of Al, Fe and Cr were found. After prolonged storage only the concentrations of Cr and Cu showed any further increase. It follows, then, that water remains pure only when stored for short periods. The advantageous adsorption and desorption properties of high-pressure polythene (low-pressure polythene is entirely unsuitable) and of Teflon towards inorganic ions should not be allowed to obscure the fact that other types of interferences may be introduced. Polythene especially, even after suitable treatment, releases organic reducing substances with the result that ions in higher oxidation states (e.g., CrO_4^{2-}, MnO_4^-, Ce^{4+}, BrO^-) are rapidly reduced. It is also known that solutions of ammonia stored in polythene become more dilute with time. Impurities found in solutions that have been kept in polythene sometimes cause interferences in ultraviolet spectrophotometry,[98] and in many electrochemical methods of analysis.[14] High phosphorus blank values have been recorded when silicomolybdic and phosphomolybdic acids are shaken with butanol in polythene vessels.[99]

More than twenty elements have been found to occur as impurities when low-ash filter papers are used, being either desorbed from the filter paper or introduced by dissolution of the ash during analysis. The major contaminants are Si, Ca, Mn, Pb and Zn.[19]

Reagents

In extreme trace analysis of solutions, the greatest care and attention must be paid to the reagents used, as the degree of purity obtainable varies very much from one reagent to another, and from element to element. The levels of the commonly encountered contaminants Si, Mg, Al, Ca, Mn, Fe, Ni, Cu and Pb[19] may, by appropriate procedures, be reduced to around 10^{-7}–10^{-9}%, and for less common elements even lower levels may be achieved. The preparation of reagents in a dust-free atmosphere may reduce the contamination by more than an order of magnitude. The commercially available "Suprapur" reagents as a rule do not satisfy the standards required by extreme trace analysis, since the control of impurities is usually restricted to only a few elements, and also since introduction of impurities from the storage vessel will proceed uncontrolled. The only way to be sure of the purity of a reagent is by regularly checking it, and therefore it is best whenever possible, to use only a few easily purified reagents such as, in addition to water, hydrochloric, hydrofluoric and nitric acids, aqueous ammonia, ammonium chloride, and some organic solvents.[1,3,6,12,17,18,67] Often it is sufficient to remove only the interfering impurity; special purification procedures may be devised based on combination of distillation, co-precipitation, liquid-liquid extraction, adsorption, *etc.* see *Separation of the matrix*, below.

One can reach particularly high purities with gases[100]—such as oxygen or hydrogen—which are particularly suitable for destruction of organic material (see *Decomposition methods*) or—such as helium, nitrogen and argon—are used as carrier gases.

One major problem is the storage and stability of very dilute standard solutions. The best storage conditions should be determined beforehand (see above). In addition to the phenomena of adsorption and desorption, the effect of exposure to light and to heat should be considered.[101] It is advisable to keep such standard solutions as relatively concentrated stock solutions, and to dilute them by using calibrated pipettes and standard flasks (of silica) immediately before use, or, better, to use solutions with concentrations $>10^{-4}M$ in microburettes with attached storage compartments.[1] The surfaces of all the apparatus should be equilibrated with the solution by shaking for some hours with a portion of the solution, discarding that portion, and filling up with a second portion for storage and use. It is good practice to keep the same apparatus always for the same concentrations of the same solutions, as they are then permanently equilibrated.

The purest reagents may be kept for long periods deep-frozen at $-25°$ without undergoing any change.[102] What has been said about attainable purity of reagents and solutions applies equally to electrode materials, *e.g.*, mercury and graphite for use in electrochemical separation procedures and inverse voltammetry, or to graphite and high-purity metals (Al, Cu, Au) to be used as electrodes for solution spectrography. It may be assumed that graphite used for electrodes contains, apart from some silicon and boron traces, no impurities in its core. Surface contamination is best removed by heating for a short time in an inert atmosphere in an induction furnace at 2500–2700°.[103]

Loss and volatilization

Even at room temperature, solutions of mercury(II) containing reducing agents lose mercury to the atmosphere. This loss can be prevented by adding a small excess of some oxidizing agent such as permanganate.[104]

Volatile chlorides of, for example, Hg^{2+}, Sb^{3+}, As^{3+} and Se^{4+} tend to be lost from hydrochloric acid solutions, and in contrast, Cr^{3+} tends to be lost from perchloric acid solutions at temperatures above 150° through formation of chromyl chloride. Slight differences in volatility of chlorides are found when samples are fumed with perchloric or sulphuric acid, for example with As^{3+}, Sn^{2+}, Ru and Os.[19] In some cases the fluorides and bromides behave differently. When metals are dissolved in non-oxidizing acids, some elements, including Si, P, As, Sb and S, may escape as hydrides. Traces of boric acid volatilize even evaporation of aqueous solutions, but the loss can be reduced by addition of mannitol or glucose.[19] Of course the problem of loss by volatilization is one which becomes much more serious when methods of dissolution and attack at high temperature have to be employed and in such cases must be given due consideration.

PREPARATION OF SAMPLE

In principle all stages in the preparation of the sample, including sample-taking, transport, storage and processing, should be considered in an assessment of the sources of error. The following example will illustrate the problem of storage. The carbon content of metal powders can be increased markedly when they have been stored for a length of time in plastic foil; the carbon in the plastic migrates on to the very large surface area of the metal powder.[105] The same applies to the chlorine, sulphur and antimony contents after storage in plastic foils containing these elements, or in rubber.[106]

Mortars and grinding vessels made of porcelain, agate and sintered corundum *etc*, contaminate samples as a result of wear;[16,19] only vessels made of crystalline corundum or boron carbide are effectively resistant to wear.[67] Solid samples should therefore at most be broken into coarse pieces, and never pulverized, even if this results in a much longer digestion being needed to dissolve the sample. Larger metal samples are best broken up in a spark-erosion machine, with electrodes made out of the sample to be analysed, or by irradiation with a laser beam[107] or, if they are very hard, by cutting with a diamond saw. Brittle materials should be wrapped in polythene film and crushed with a few hammer blows. The coarse pieces must then be etched with purest hydrochloric, hydrofluoric or nitric acid (or their mixtures), depending on the sample, in order to loosen and remove impurities trapped on the surface during the crushing.[102] Care must be taken during the final rinsing with high-purity water, and drying, that no contamination is introduced from impurities in the air. Surfaces can also be cleaned by bombarding them with noble gas ions, usually argon.

Organic samples such as biological material or food should not be ground up, but if this is unavoidable, the sample should be deep-frozen, and ground in a silica mortar cooled by liquid air. Liquid samples such as blood, vaccine and urine may be concentrated by freeze-drying.[108–110]

OPENING-OUT PROCEDURES

Before enrichment or separation of the trace elements sought, the sample must be brought into solution, and decomposition methods are usually used. The optimum conditions for decomposition are a favourable ratio of the sample amount to surface area of crucible, only a small excess of reagents which can be easily purified, and work in a clean atmosphere. Volatilization of elements must be prevented, or allowed to proceed quantitatively so as to provide a means of separating these elements. Exchange reactions between the melt or the solution and the vessel surfaces should be minimized. Volatilization of many elements, whether as such or as halides, oxides or hydrides, is conveniently studied by use of radioactive isotopes.[111,112]

The dissolution or fusion of inorganic matrices is naturally associated with more problems than for organic materials, which is evident from the sometimes completely different procedures used.

Inorganic matrices

When dealing with the opening out of inorganic matrices account must be taken of the numerous matrix elements and their possible combinations, with the result that a great variety of methods has to be used.[16,111,348] Most pure substances will dissolve in acids or mixtures of acids (Table II) though some will volatilize in the process, allowing determination of trace elements in the residue.[67] In some cases a metal matrix may be separated very elegantly by volatilization as an organometallic compound as for example aluminium[113] in determination of traces of the alkali metals in pure aluminium. Conversely, volatile trace elements may be separated from a non-volatile matrix by distillation in a quartz or Teflon apparatus and transferred with or without the aid of a carrier gas to a receiver, as for example, Si,[36,114] Cl,[115,116] Re,[117] Os, Ru,[118–120] As,[16,36] or Se.[121] Gas evolution methods have proved themselves suitable also in determinations of sulphur[16] and of arsenic.[16,122,123]

Much more difficult is the opening out of acid-insoluble materials such as quartz, silicates, many minerals and ores, which can only be brought into solution by fusion or sintering methods (Table III). Very high blank values are often introduced by the solid fusion mixture, which can only be purified with difficulty, and which attacks the crucibles at the high temperatures used. The crucible material must also be carefully chosen as it may sometimes react with the trace elements. Losses as spray or from spitting can be avoided by taking special precautions.[1]

Fusion and sintering procedures have very limited usefulness in extreme trace analysis, and decomposition in the gas phase (Table IV) is much more important. Gases can be prepared in a very high state of purity, and the very pure silica used for the reaction vessels (Fig. 4) shows little tendency to react with the volatile reaction products. Only in a few cases—mainly at very high temperatures—do products diffuse into the silica surface.

Special decomposition procedures are used in the conventional determinations of gases, carbon, sulphur, *etc* in high-purity metals. Samples are melted or burned in

TABLE II.—ACID DECOMPOSITION METHODS FOR HIGH-PURITY INORGANIC MATERIALS

Acid used for decomposition	Matrix		Crucible material	Volatile trace elements*	Remarks
	non-volatile	volatile			
HCl	Be, Al, Ga, In, Zn, Fe, U, Th, Cr, S.E.	As, Sb, Sn	Silica Teflon	Hg, B, Si, Ge, Sn(IV), P(III) As, Sb, S(II),[19] Se,[121] Re.[278]	HCl may be obtained in an extremely high state of purity.[279]†
HBr	Tl, Cr	Ge, As, Sb, Sn,[280] Se[121]	Silica Teflon	Hg, B, In, Si, Ge, Sn, As, Sb, Se, Re.[1]	HBr may be obtained in a high state of purity.[279]†
HI + HCl + H_3PO_2	various		Silica	S	Conversion into H_2S.[16]
HF + $HClO_4$	Ti, Zr, Hf, Cr, Nb, Ta, W	B, Si, Ge	Teflon	B, Si, Ge, As, Sb, Mn, Re,[1,281] Se,[121] Cr,[282]	HF may be obtained in a high state of purity.[283,284]
HF + H_2O_2	Nb, Ta, Mo, W		Teflon		For Kjeldahl nitrogen determination.[95]
HF + HNO_3	Nb, Ta, Mo, W, Ti		Teflon	Se,[121] Cr[282]	Best decomposition method.[285]‡
HNO_3	Cu, Ag, Pb, Bi, Hg, Te, Ga, Tl, V, U, Cd		Silica	Se,[121] Hg,[112] Ru,[118]	HNO_3 may be obtained in high purity by distillation in a Teflon apparatus.[286]
HNO_3 + HCl	Au, Pt metals, Mo	Ge	Silica	Se,[121] Hg,[112]	
$HClO_4$	U, V		Silica	Se,[121] Hg,[112] Cr,[282] Re,[278] Ru, Os,[118,119]	

* Does not necessarily imply complete loss.

† Evolution of hydrogen may cause loss of certain other elements.

‡ Decomposition under pressure in a Teflon coated bomb avoids losses of volatile trace elements.[298,338,339]

TABLE III.—FUSION AND SINTERING PROCESSES FOR INORGANIC MATRICES

Reagents	Fusion temperature °C	Crucible material	Trace elements lost*	Remarks
Na_2CO_3 $Na_2CO_3 + K_2CO_3(2:1)$	850 720	Platinum Platinum	Se,[121] Tl, Hg,[111] and others	Corrosion of platinum is less when heated in a CO_2 atmosphere.[287]
NaOH	400	Zirconium better than silver[288]	Se,[121] Hg,[111] and others	Corrosion of platinum is less when heated in an N_2 atmosphere.[289]
$Na_2B_4O_7.10\,H_2O$	1000	Platinum	Se,[121] Hg,[111] and others	Dissolve the solidified melt in HF.[290]
$K_2S_2O_7$	420	Silica,[291] platinum	F[292]	Quartz is attacked less than platinum.[291]
$K_2S_2O_7 + KHF_2$	700	Platinum	Zr,[294]	
$B_2O_3(+LiCO_3)$	1200	Platinum	Hg,[111] Se,[121] and others	
$Na_2O_2 + Na_2CO_3$	250–700	Zirconium, platinum nickel	Hg, Se, Tl, Cr, As, Re[1]	Zirconium suffers little corrosion,[295,296] but interferes more than platinum.[297]
$Na_2CO_3 + KNO_3$	390	Platinum	Se, Hg[298]	Also suitable for organic matrices.[298]
Na_2CO_3 + borax + PbO + starch	900	Porcelain	Ag,[299] Rh,[120] Ir,[300] Ru,[301] Os[302]	Enrichment process for fire-assay.[120,303]
$Na_2CO_3 + S$		Porcelain	Hg[111]	Freiberger flux.
$Li_2B_4O_7.5H_2O$ $LiBO_2$	 800	Platinum Platinum	Hg[111]	Preparation of samples for X-ray fluorescence and spectrographic methods.[304,305]
$LiF + H_3BO_3$[306]	800–850	Platinum		Particularly suitable for the decomposition of silicates before atomic-absorption detn. of Zn, Mn, Pb, Mo, W, Ti, Zr, Hf.[307]
$Na_2CO_3 + ZnO$	800	Platinum, corundum	Se,[121] Hg,[111] and others	
$Na_2CO_3 + MgO$		Platinum		Eschka mixture
$CaCO_3 + NH_4Cl$	1000	Platinum	Se[121]	Lawrence Smith decomposition.

* Does not necessarily imply complete loss.

TABLE IV.—DECOMPOSITION OF INORGANIC MATRICES IN THE GAS PHASE

Gas used	Temperature, °C	Apparatus made from	Additive	Matrix		Elements to be determined	Remarks
				non-volatile	volatile		
O_2, N_2, H_2	700–1300	Silica tubing	Graphite	MnO_2, Al_2O_3, Fe_2O_3, and others		Zn,[308] Tl,[309] Pb,[310] Cd,[311] Be[312]	Vaporization analysis. See Fig 4.
O_2	315	Silica tubing		Cu and others		Se[313]	
H_2		Silica tubing		Al, Ga, In		Zn[314]	
O_2	800	Silica tubing	CuO	Metals		Re[315]	
	<1400	Silica tubing	CuO	Metals		C,[316] S[316]	
	>1500	Silica tubing		Nb, Ta, W		C,[95] S[95]	High-frequency excitation.
H_2	800	Silica tubing		Mo, W and others		S,[317] O, Cl	
Cl_2	<600	Silica tubing		Ta		Mo, V,[318]	
		Silica tubing			Ga[319]	Cu, Au	
	>600	Silica tubing		Cu, Ag, Co	Be, Ti, Zr, Hf, As, Sb, U, Sn, Nb, Ta, and others	Rare earths, Th, SiO_2[111]	
CCl_4	900	Silica tubing			W,[320] Mo,[321] Ge,[322] V, As, Sb, Fe[111]	non-volatile chlorides	
H_2O	900	Silica, platinum	WO_3	U and others		F[111,328]	
	1100	Silica	U_3O_8	Zr and others		B[324,325]	Pyrohydrolysis
	1100	Silica	V_2O_5	Ti and others		Cl[326]	
HBr/H_2SO_4		Silica tubing			Cu, As, Co	As, Sb, Sn, Se[327]	
HF/HNO_3	110	Teflon tubing			Si,[328,329]	non-volatile fluorides	Vapour-phase
NO_2	850	Silica tubing			Fe, Co, Ni[330]		

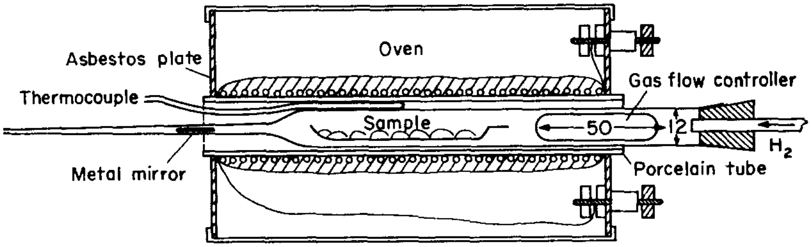


FIG. 4.—Arrangement for gas-phase distillation.[310] The volatile element or a volatile compound of the element is driven off from the sample by heating in a suitable atmosphere.

an atmosphere of pure carrier gas in tubes made of silica or "Pythagorasmasse" (a high-temperature porcelain), sometimes with flux added. As container materials and fluxes can raise blank values substantially, it is preferable, in order to achieve very low limits of detection, to use high frequency (3–6 MHz) induction heating[95] or to fuse the sample without a container by suspending it free in a specially shaped high-frequency field.[124]

Organic matrices

The majority of organic materials, being composed of only a few elements, are readily ashed dry, or according to procedures outlined in Table V.[112,125–127,348] About half of the procedures in the literature use liquid reagents and relatively low temperatures to achieve decomposition, so that losses through volatilization, adsorption and reaction with vessel materials are limited to only a few elements. For this reason, substances particularly difficult to decompose are occasionally not completely mineralized, or require such a large amount of reagent that the blank value exceeds the permissible limit.

Of the reagents under consideration nitric acid and hydrogen peroxide are available in highest purity. Detailed instructions have been published which effectively ensure that easily volatile elements are retained, and that a minimum amount of reagent is required.[128,339,348]

The oldest and simplest method of dry ashing by heating in a muffle furnace at 400–800° in the presence of air can lead to more or less loss of many elements, including Hg, B, Pb, Zn, Cd, Ga, In, Tl, As, Sb, Fe, Cr and Cu. The addition of fluxes such as sulphur, phosphates, or sulphuric acid, reduces the losses in many cases,[6] but magnifies the risk of raising the blank value. Interaction between the flux and the vessel—such as formation of insoluble silicates from silica and porcelain—and the formation of difficultly insoluble oxides, cause losses which, together with the other disadvantages, render these procedures unsuitable for extreme trace analysis.

Combustion in the oxygen-flask[129–132] offers advantages when readily volatilized elements such as halogens, S, Se, P, B, Hg, As and Sb are to be determined. But for complete combustion of 1 g of material a flask of about 10 l. is required, and hence there is a serious increase in the magnitude of the adsorption errors. A modification of the so-called static combustion procedure, well-tried in micro-elemental analysis, permits the determination of many elements, both volatile and non-volatile, in the nanogram region in samples weighing less than 0·3 g.[133]

Up to 2 g of organic matter may be burned in a 200-ml calorimeter bomb filled

TABLE V.—WET-ASHING PROCEDURES FOR ORGANIC MATRICES

Reagents	Matrix	Remarks
$H_2SO_4 + HNO_3$	plants	The most common procedure; danger of loss of As, Se, Hg and others by volatilization.[6]
$H_2SO_4 + H_2O_2$	plants	Pb is lost by co-precipitation with $CaSO_4$.[331] Ge, As, Ru and Se are also lost.[332]
HNO_3	biological samples	HNO_3 is easily purified; decomposition temperature of 350°.[6] Short reaction time, metal nitrates are soluble.[6,125,333–335] In a PTFE-bomb[338,339]
$HNO_3 + H_2O_2$	biological samples	A rapid decomposition method for small samples at low temperature.[335]
$HClO_4$	biological samples	Catalysts such as $(NH_4)_2MoO_4$ may be added.[6,112]
$H_2SO_4 + HClO_4$	biological samples	Only suitable for small samples.[6,112,348] Explosion danger!
$HNO_3 + HClO_4$	protein and carbohydrate (no fats)	Less danger of explosion; no loss of Pb.[6,112]
$H_2SO_4 + HNO_3 + HClO_4$	universally applicable, even fats and soot	No danger if the temperature is carefully controlled. As, Sb, Hg, Au, Fe and some other elements are volatile; ashing should be done under reflux.[6,112,335,336]
$HCl + KClO_3$	biological samples	Not suitable for trace analysis as too many elements may be lost by volatilization.[6]
$H_2O_2 + Fe^{2+}$	widely used (except fats, oils, dense plastics and carbon)	Ashing occurs through formation of OH radicals, and at about 100°, so there is minimum danger of loss through volatilization. Particularly useful for large samples, and in control of environmental radioactivity.[337]

with oxygen to a pressure of 30 atmospheres. With this apparatus, 1 μg of selenium has been recovered quantitatively by releasing the pressure very slowly after the combustion and passing the gaseous products through a suitable absorption train.[121]

Combustion in a stream of oxygen, so widely employed for determinations of elements forming volatile oxides and other products, requires that a slow, controlled combustion be achieved in order to minimize problems associated with the absorption of the products. Significant improvements on the simple arrangement of silica or Supremax combustion tubes[134,135] are offered by the principle of controlled combustion rate developed by Rademacher and Hoverath.[136]

Special apparatus has been described for handling the combustion of inflammable liquids such as petrol and paraffin.[137,138]

Far and away the best conditions for extreme trace analysis are offered by "low-temperature ashing".[139–142] The sample is slowly burned in a stream of oxygen at a pressure of 2–5 mmHg, excited by a high-frequency field of 300 W at 13·56 MHz, with the temperature between 100 and 200°. Elements still volatile at these low temperatures, such as Ag, Au, Hg, Se and I, may be trapped in a suitable receiver.

This principle has been further adapted by the author and his co-workers[143] to the peculiar requirements of extreme trace analysis: the combustion is carried out in a special, small silica reagent tube fitted with a cold finger (Fig. 5). Excitation of the oxygen is achieved in a microwave resonant cavity operated at 2450 MHz with variable

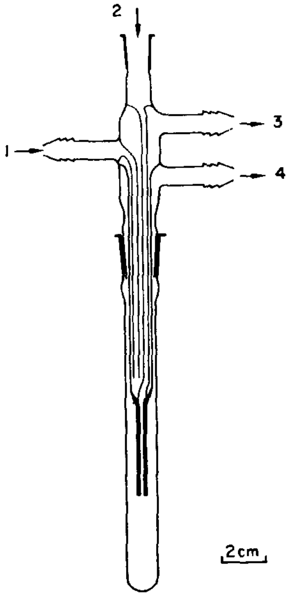


FIG. 5.—Decomposition vessel for cold-ashing of organic matrices before the determination of extremely small amounts of trace elements.[148]

1 Water inlet	3 Water outlet
2 Oxygen stream	4 Vacuum

power up to 200 W (Fig. 6). With this source, practically all organic matrices, including plastics, slimes, soot and so on, in amounts up to 1 g, can be completely decomposed, and nanogram amounts of volatile elements may be recovered with yields >98%, With a slightly different apparatus it has proved possible to obtain recoveries of mercury above 91%, also at the nanogram level. This procedure is thus an ideal decomposition technique which, in combination with very sensitive methods of

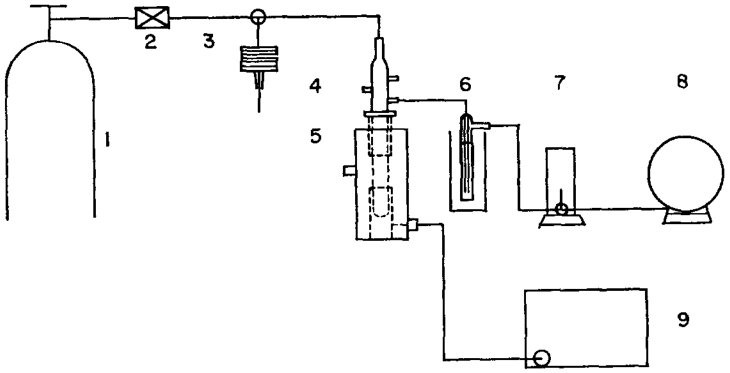


FIG. 6.—Schematic arrangement of the apparatus for cold-ashing of organic matrices.

1 Oxygen cylinder	5 Resonant cavity
2 Needle valve	6 Cold trap
3 Bleed capillary and air filter	7 Mercury manometer
4 Decomposition vessel	8 Vacuum pump
9 Microwave generator	

TABLE VI.—EXAMPLES OF SEPARATION BY CO-PRECIPITATION

Trace element	Matrix	Collector precipitate	Remarks
Se, Te		$Fe(OH)_3$, $Al(OH)_3$, $MnO(OH)_2$	pH 5, strongly time-dependent[121,340]
Te		As	$6M$ HCl + H_3PO_2[340]
Tl		$MnO(OH)_2$	NH_3 in presence of Mn^{2+} and H_2O_2[309]
Cr		Eriochrome Black T + Fuchsin	pH 5·5[282]
Mo	W	Sb_2S_5	Precipitation from tartrate solution with thioacetamide[341]
Pb	Bi, In, Tl	$SrSO_4$	4–$8M$ HNO_3[174]
Ag	Cu	TlBr	$4M$ HNO_3[174]
Hg	Ag	AgI	In presence of EDTA[165]
Se	Ag, Ni, Cu, Co	$Bi(OH)_3$	pH 10–11[174]
Sb, Bi, Pb, Sn	Ni	$MnO(OH)_2$	pH 2–3, Mn^{2+} + MnO_4^- at 70°[342]
Zr, Nb, Ta and others	Mo, W	$Fe(OH)_3$	pH 12[343]
K	Na	Ammonium tetraphenylborate	pH 5, NH_4^+ + $NaB(C_6H_5)_4$[344]

determination, should find wide application in the field of extreme trace analysis applied to forensic and medical science.

Combustion in an oxy-hydrogen flame[144–146] is widely employed in determination of traces of halogens, sulphur, selenium and nitrogen. Pyrolytic decomposition in hydrogen is also becoming more widely used, for example, before determination of traces of carbon, nitrogen, phosphorus and sulphur.[147–149]

SEPARATION OF THE MATRIX OR THE TRACE ELEMENTS

From what has so far been said it can be seen that there is only some point in carrying out a separation of the matrix material, or of the trace elements, when the method of physical measurement does not itself offer adequate selectivity, when calibration problems arise through non-availability of suitable standards, or when the determination of a large number of trace elements in one sample—particularly in ppm microanalysis—is called for. In the last case separation schemes which isolate each individual element are necessary. Separation procedures are also indispensible when traces of elements are to be determined by rather unselective chemical techniques such as kinetic methods, or when the limit of detection can be significantly lowered through the use of multiplication techniques[150,151] as in the determination of titanium,[152] silicon,[153] or phosphorus[154] in terms of the molybdenum in the corresponding heteropolymolybdate.

The ideal separation method should offer a large distribution coefficient, rapid equilibration, minimal interferences at the phase boundary, and low blank values. Only a few typical examples can be given here, from the many possible combinations of decomposition and separation methods which are now in use.

Volatilization methods

These methods are particularly attractive because of the very low associated danger of contamination from reagents. Usually separation occurs simultaneously with the decomposition step.

The matrix element can be separated by evaporation (organic solvents, water, sulphur, iodine, mercury, *etc*) by formation of volatile organometallic compounds (*e.g.*, aluminium,[113] gallium,[155] beryllium[156]) or oxides (B, C, Se, Re, Os, Ru) or by distillation of chlorides (Si, Ge, Se, Te, P, As, Sb, Sn, *etc*).[67,157] Traces can be separated as the element (Hg,[158,159,160] In, Cd,[158]), as volatile compounds ($GeCl_4$, $AsCl_3$, SeO_2, CrO_2Cl_2, As_2O_3,[1,157,161] as bromides of Sn, As, Sb, Se and Re,[162]) as oxides (OsO_4, RuO_4,[119] Mn_2O_7,[163]) or as gaseous compounds (BF_3, SiF_4, H_2S, SO_2, H_2Se, CO_2, AsH_3, PH_3, NH_3, *etc*)[1,161] The determination of nitrogen in high-purity niobium will serve as an example of how experimental conditions may be optimized.[159]

With the normal Kjeldahl method a limit of detection somewhat over 1 ppm may be achieved,[101] mainly because of high blanks from reagents and the laboratory air, and the rather large volume of solution resulting from the steam distillation of the ammonia. The limit of detection may be reduced by almost two orders of magnitude when the sample is attacked in a nitrogen-free argon atmosphere with a mixture of hydrofluoric acid (purified by distillation in a Teflon apparatus) and hydrogen peroxide. A closed-circuit distillation apparatus (Fig. 7) was developed for the final separation of the ammonia. The steam for the distillation is produced in the absorption vessel. Specially purified absorption solution and sodium hydroxide solution

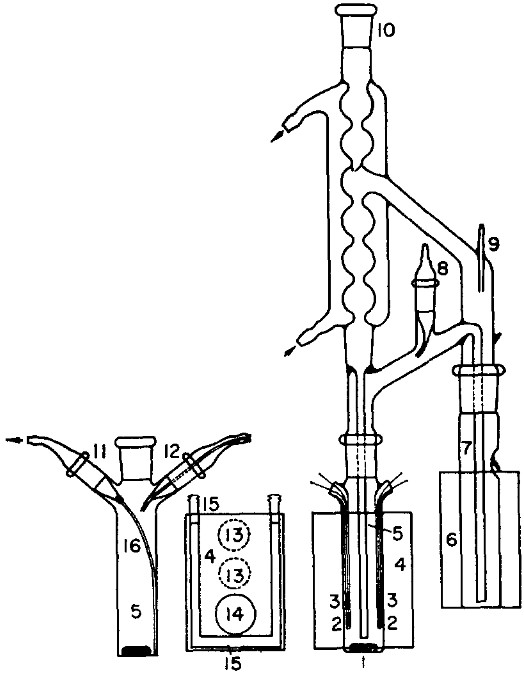


FIG. 7.—Closed-circuit distillation apparatus for the separation of very small amounts of ammonia after a Kjeldahl decomposition.[159]

1 Magnetic stirrer
2 Generator electrode (Pt)
3 Indicator electrode
4 Aluminium block
5 Titration vessel (side view)
6 Aluminium block (top view)
7 Sample vessel
8 Solvent inlet (0·1*N* H_2SO_4)
9 Inlet for 30% NaOH soln.
10 Joint for absorption tube
11 Tube for removal of sample
12 Buffer soln. (KBr, $Na_2B_4O_7$)
13 Holes for heater elements
14 Hole for titration vessel
15 Cooling water pipe
16 PTFE capillary tube.

are taken through magnetically-operated valves direct from storage vessels protected from the atmosphere, so that the very low blank value may also be kept constant. The volume of the absorption solution is kept constant at about 2 ml during and after the distillation by balancing the heating of the two flasks. The ammonia is determined directly in the distillation apparatus by coulometric titration with bromine generated *in situ*, with biamperometric end-point detection. As the standard deviation is less than 10 ng, nitrogen at the 1 ppm level may be determined with reasonable accuracy in 100-mg samples.

Precipitation methods

Few successful applications of precipitation as a means of separating a matrix without at least partial co-precipitation of trace elements have been described.[67] A systematic investigation has been made of silver as a matrix.[164] The ions of other metals which normally tend to be absorbed on silver halide precipitates—such as Bi^{3+}, Cd^{2+}, Hg^{2+}, Pt^{2+}, Pd^{2+}, Tl^{+} and Tl^{3+}—will not be co-precipitated if they can be masked as sufficiently stable undissociated molecules or complexes, and quantitative separation of traces of Cd, Pd and Hg from Ag is in this way made possible. The separation of traces of mercury succeeds only under carefully controlled conditions.[165]

One of the exceptions concerns the electrolytic deposition of a number of matrix materials (*e.g.*, Cu, Pb, Zn, Cd, Ni, Co and Fe) at controlled potential on a mercury cathode.[67,166–168] Trace elements, including Be, Al, Ti, Zr, Hf, U, Nb, Ta, W, B, S and P, remain quantitatively in the solution. Conversely, of course, trace elements may be separated from matrix elements of the second group, by electro-deposition on platinum,[67,169] graphite[170] or mercury cathodes,[67] before their subsequent determination.

Radiochemical yield determinations have shown that over 90% of nanogram amounts of Zn, Co and Fe in Nb, Ta and W matrices (in amounts over 100 mg) can be deposited on a mercury cathode and recovered by vacuum distillation of the mercury.[171] Noble metals, either as traces or as matrices, can be deposited on mercury or other less noble metals without the application of any external potential.[67,172,173]

Co-precipitation of traces of elements on suitable collectors has been well studied.[14,67,157,161,174] Co-precipitation may usually be attributed to co-crystallization adsorption, colloid-interactions, or occlusion.[161,174] The collector material—generally a metal sulphide or hydroxide, or an organic reagent—should co-precipitate the trace ion quantitatively but not interfere in the subsequent determination, and should itself be selectively precipitated, in the presence of complexing agents if need be. Organic collectors composed, for example, of a large dyestuff cation (Methylene Blue or Rhodamine B) and a large dyestuff anion (Methyl Orange) offer a number of advantages. The salts are only sparingly soluble in water, they co-precipitate many heavy metals quantitatively and, as they are purely organic, they are readily destroyed and completely removed by mineralization.[175,176] The separation factor (again readily determined by radiochemical tracer methods) depends on the type of collector and the amount used, the presence of foreign ions and complexing ligands, the order of addition of reagents, the acidity, the time of standing of the precipitate, and the temperature. All of these factors should be optimized for a given problem. The well-established theory of precipitation processes allows suitable choice of collector and precipitation conditions.

Liquid-liquid extraction procedures

Solvent extraction methods[6,67,157,161,177–189,190] rank among the most important and most widely used separation methods, partly because the Nernst distribution law is obeyed by most systems down to very low concentrations,[191] and also because nearly every ionic species can form at least one extractable entity such as an undissociated compound, solvated species, ion-pair, chelate, and so on. Synergic effects[178,192,193] which have been shown to occur in some combinations of solvents, add to the number of possibilities.

Matrix elements[194] or traces can be separated, either in groups or individually, and in extremely low concentrations.[6,67,195,347] In contrast to precipitation methods, adsorption at phase boundaries presents no problem in extraction methods and furthermore, equilibrium is usually attained very rapidly. When the distribution coefficient is sufficiently large, large volumes of aqueous solution may be extracted with very small volumes of organic solvent, thus effecting a considerable gain in concentration.

The extracted elements can be submitted to quantitative determination after evaporation of the organic solvent, or following a back-extraction into an aqueous solution. Occasionally small amounts of organic solvent remaining can cause interferences in electrochemical determinations, and in such cases they must be destroyed by fuming with nitric and perchloric acids.

The selectivity of certain reagents together with the possibilities offered by variation of oxidation state, pH, solvent, and addition of masking reagents allow the creation of numerous separation schemes[196–202] by means of which up to forty components can be completely separated from a single mixture, so as to permit their subsequent determination. Such procedures are indeed valuable in ppm-microanalysis when many elements must be determined in just one 100- mg sample.[203]

Solvent extraction methods can of course be combined with other separation procedures, particularly co-precipitation[67,204–209] and ion-exchange.[210–211]

If the extractable ion is also coloured a direct spectrophotometric determination becomes an obvious choice.[179] Sometimes it is possible to determine ions directly in the organic phase polarographically after addition of a suitable electrolyte. Substoichiometric extraction methods[64] are finding increasing application in activation and isotope-dilution analysis.

Ion-exchange procedures

These procedures[67,212–223] are universally applicable to the separation of ions of opposite charge (cation–anion separations) and of like-charge ions (ion-exchange chromatography) both for matrix–trace separations and for handling mixtures of trace ions. Cation- and anion-exchangers based on organic polymers are to be preferred, used either in columns or as impregnated papers[224,225] and with aqueous or organic solvents.[222] Anion-exchanger resins make possible good separations of transition elements as anionic complexes.[226] Combined ion-exchange–extraction procedures in which some species out of a group of ions are selectively held on a resin and then eluted into an organic phase have proved useful in certain problems.[223] Liquid ion-exchangers offer further possibilities.[178,227]

Small beads of ion-exchange resin of reproducible size and loaded with one particular ionic species are useful as a means of standardizing trace analytical procedures.[228] Redox exchangers[228] have been used for the preparation of oxygen-free water, and for the removal of peroxides and metal ions from organic solvents.

Chelating ion-exchange resins[229] have many applications in trace analysis, though only a few extensions to extreme trace analysis have been described, such as for example, the enrichment of gold in natural waters.[230] The same can be said for ion-exchange resin membranes,[231] which have been used for the separation of traces of boron in silicon,[232] or of trace elements in biological samples.[233]

When ion-exchange resins are used to extract only the trace ions, a large volume of sample solution can be poured through a relatively small column with low exchange capacity, or just filtered through a paper impregnated with ion-exchange resin. In addition to separation, enrichment is achieved by eluting with a small volume of solution. In such cases it should be remembered that the distribution coefficients of the trace ions between solution and resin are appreciably smaller in the presence of large amounts of other ions than for pure, dilute solutions.

In the case of retention of the matrix ions by the resin the trace ions will remain in a rather large volume of solution and will have to be concentrated by boiling down the solution, which in turn adds to the sources of error. In addition, when large amounts of matrix material are held on the resin, the capacity is rapidly exhausted and the distribution coefficient falls. The answer to this problem lies simply in the use of sufficiently large columns of adequate capacity.

The use of ion-exchange resin in extreme trace analysis is limited by two sources of error: irreversible adsorption of small quantities of material, and contamination of the eluate by the resin (traces of iron, for example, or organic material such as the resin itself). Organic impurities particularly affect electrochemical methods. Sometimes the interferences can be reduced by pretreatment of the column with suitable acids or bases, by a change of elution conditions, by use of radio-active isotopes[234] (dilution analysis), by ashing the resin and determining the trace ions in the ash (*e.g.*, by use of oxygen gas excited by a microwave discharge[235]) or by direct excitation of the absorbed elements on the resin, *e.g.*, with X-ray fluorescence analysis.[236–239]

Specialized separation procedures

While those techniques already discussed are as applicable to separations of macro- from micro-components as to further separations of groups of trace elements, thin-layer, paper, and gas chromatography and related techniques are certainly microchemical in scope.

Practically all ions can be separated on a sub-micro scale by thin-layer chromatography.[240–242] Extremely thin films of metal oxides (less than 20 μm thick) deposited by evaporation *in vacuo* (*e.g.*, of In_2O_3[243]) or by anodic oxidation of metal plates such as aluminium, have been used for thin-layer chromatographic separations of sub-microgram amounts of many ions.[240–242] Metal chelates such as dithizonates and dithiocarbamates have been separated and determined in picogram amounts on 6-μm thick alumina films.[244] The limit of detection can be lowered even further by procedures such as the following: metal chelates with polychlorinated xanthates (*e.g.*, hexachlorobicycloheptene derivatives) may be separated by conventional thin-layer chromatography, and the metals determined indirectly after thermal decomposition of the chelates, as the polychlorinated alcohol is detected by GLC with an electron-capture detector, with sufficient accuracy even at levels of less than 1 ng.[245]

The possibilities of paper chromatographic and electrophoretic separations of elements in microgram amounts will not be discussed in this review. Usually the limit of detection for these techniques is no lower than 100 ng. The ring-oven technique[246] and others developed from it are well suited to rapid separations of trace elements[247,248] when the matrix has already been removed by some other method. Under certain circumstances the technique may be coupled with the use of isotope exchange reactions to permit determination of elements in nanogram amounts.[249–251] A paper chromatographic separation employing a specialized technique[252] permits the separation of trace elements from a matrix with an enrichment factor of 10^4.

Though gas chromatographic separations of metal chelates[33,253–256] and of non-metals in the form of compounds formed from anions[257,258] are possible, separations at the nanogram level are beset by many problems. On the other hand isolated determinations such as those of beryllium[259–261] and chromium[262] with trifluoroacetyl-acetone,[259–261] nickel, zinc and others with polychlorinated xanthates,[245] selenium as selenate esters formed from SeO_2 and certain polychlorinated alcohols[263] or as 5-chloropiaselenol,[264] can be achieved either directly or indirectly by use of special detectors after separation by gas chromatography.[345]

In choosing the type of column precautions should be taken to avoid any irreversible exchange reactions with the stationary phase. Special techniques are necessary for concentrating, evaporating, and injecting μl volumes of solutions on to the column.[245]

Gas chromatographic methods are of great importance in the determination of very low levels of impurities in gases[265] and of gases and non-metals (H, C, O, N, S, P and others) in solids such as metals and semiconductors. Gases (*e.g.*, H_2, N_2) isolated from the matrix or gaseous reaction products such as CO_2 CO, SO_2, H_2O, NH_3, H_2S, *etc*[95,266–268,346] may be separated by gas chromatography and determined in amounts less than a nanogram with suitable detectors.[269–271]

A number of separation procedures based on selective freezing out, absorption or diffusion (*e.g.*, of hydrogen through palladium[100] or of helium through silica or certain glasses[272]) complete the range of techniques available for gaseous samples.

Zone-refining[273] has been shown in recent years to offer interesting possibilities for the enrichment of trace impurities in high-purity materials without the use of additional reagents,[283,274] and also, in contrast, for the separation of "impurity" metal chelates from large excesses of the pure reagent,[275,276] for example, from 8-hydroxyquinoline.

Acknowledgement—I should like to thank Dr. I. L. Marr, Aberdeen, for his kindness in translating this paper into English, my colleagues Dr. E. Grallath, Dr. V. Krivan, and Dr. P. Tschöpel for their helpful criticism, and Miss I. Lorenz and Miss U. Nagorny for their assistance in preparing the manuscript.

Zusammenfassung—Bei der Bestimmung von Elementgehalten im ppM-Bereich in anorganischen und organischen Matrices helfen Lösungsverfahren, Eichprobleme zu vereinfachen und Nachweisgrenzen zu senken. Der erste Teil des Übersichtsreferates behandelt unter Berücksichtigung von ca. 350 Literaturstellen und Erfahrungen des Autors auf diesem Gebiet die vielfältigen Methoden zur Probenvorbereitung, zum Lösen der Proben und zur Isolierung von Spurenelementen vor ihrer Bestimmung und die Problematik der Fehlerreduzierung bei diesen gegenüber direkten Bestimmungsverfahren zusätzlichen Operationen.

Résumé—Dans le dosage d'éléments au niveau de la ppM dans les matrices minérales et organiques, les techniques en solution sont utiles parce qu'elles simplifient les problémes d'étalonnage et améliorent la limite de détection. L'auteur passe en revue, à la lumière de sa propre expérience, quelques 350 publications traitant de méthodes de préparation et de dissolution d'échantillons et de l'isolement d'éléments à l'état de traces avant leur dosage. Les erreurs dans ces méthodes, rendues plus difficiles à réduire à cause des opérations supplémentaires exigées, sont comparées à celles associées aux méthodes plus directes.

REFERENCES

1. G. Tölg and I. Lorenz, *Fortschr. Chem. Forsch.*, 1969, **11**, 507.
2. G. Tölg, *Analyst*, 1969, **94**, 705
3. J. H. Yoe and H. J. Koch Jr., *Trace Analysis*, p. 645. Wiley, New York, 1957.
4. D. Monnier, *Chimia*, 1959, **13**, 314.
5. I. P. Alimarin, *Zh. Analit. Khim.*, 1963, **18**, 1412; *J. Anal. Chem. USSR*, 1963, **18**, 1229.
6. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, Springer-Verlag, Berlin, 1964.
7. J. P. Cali, *Trace Analysis of Semiconductor Materials*, Pergamon, Oxford, 1964.
8. G. H. Morrison, *Trace Analysis*, Interscience, New York, 1965.
9. J. Minczwski, *Chim. Anal.*, 1965, **47**, 401.
10. J. Swietoslawsky, *Chem. Analit.* (*Warsaw*), 1966, **11**, 617.

11. E. Rexer, Editor, *Reinststoffprobleme, Bd.* II *Reinststoffanalytik*, Akademie Verlag, Berlin, 1966.
12. H. Specker, *Z. Anal. Chem.*, 1966, **221**, 33.
13. W. W. Meinke and B. F. Scribner, *Trace Characterization, Chemical and Physical*, National Bureau of Standards, Monograph 100, Washington, 1967.
14. R. Neeb, *Spurenanalyse*, in *Die analytische Chemie in der erzeugenden und verarbeiten Hüttenindustrie*, pp., 151–170. Verlag Stahleisen Düsseldorf, 1968.
15. P. W. West and F. K. West, *Anal. Chem.*, 1968, **40**, 138 R; 1970, **42**, 99 R.
16. I. P. Alimarin, *Analysis of High-Purity Materials*, Israel Program for Scientific Translations, Jerusalem, 1968.
17. M. Pinta, *Detection and Determination of Trace Elements*, Oldbourne, London, 1967.
18. H. J. Eckstein, Editor, *Spurenanalyse in hochschmelzenden Metallen*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1970.
19. I. M. Korenman, *Analytical Chemistry of Low Concentrations*, Israel Program for Scientific Translations, Jerusalem, 1968.
20. E. J. Underwood, *Trace elements in Human and Animal Nutrition*, Academic Press, New York, 1971.
21. A. J. Hegedüs, *Acta Chim. Hung.*, 1962, **30**, 21.
22. R. L. Hahn, *Mikrochim. Acta*, 1960, 650.
23. L. G. Young, *Analyst*, 1962, **87**, 6.
24. N. H. Nachtrieb, *Principles and Practice of Spectrochemical Analysis*, McGraw-Hill, New York, 1950.
25. H. Massmann, *Spectrochim. Acta*, 1968, **22B**, 215.
26. B. V. L'vov, *ibid.*, 1969, **24B**, 53.
27. R. G. Anderson, I. S. Maines and T. S. West, *Anal. Chim. Acta*, 1970, **51**, 355.
28. M. D. Amos, P. A. Bennett, K. G. Brodie, P. W. Y. Lung and J. P. Matousek, *Anal. Chem.*, 1971, **43**, 211.
29. G. W. Dickinson and V. A. Fassel, *ibid.*, 1969, **41**, 1021.
30. I. Kleinmann and V. Svoboda, *ibid.*, 1969, **41**, 1029.
31. R. Neeb, *Fortschr. Chem. Forsch.*, 1963, **4**, 333.
32. *Idem.*, *Inverse Polarographie und Voltammetrie*, Verlag Chemie, Weinheim/Bergstraße, 1969.
33. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon, Oxford, 1965.
34. J. Minczewski, *Zh. Analit. Khim.*, 1967, **22**, 244.
35. I. P. Alimarin and Yu. V. Yakovlev, *Zavodsk. Lab.*, 1960, **26**, 915.
36. C. J. Rodden, *Analytical Chemistry of the Manhatten Project*, McGraw-Hill, New York, 1950.
37. H. Nickel, *Physikalisch-chemische Analysenmethoden zur Untersuchung von Reaktormaterialien und Kernbrennstoffen*, *KFA-Bericht*, Jül-216-RW, 1965, 1.
38. K. H. Neeb and W. Gebauhr, *Fortschr. Chem. Forsch.*, 1969, **12**, 623.
39. H. J. M. Bowen, *Trace Elements in Biochemistry*, Academic Press, London, 1966.
40. K. M. Reese, *Anal. Chem.*, 1970, **42**, 26A.
41. K. G. Sloman, A. K. Foltz and J. A. Yeransian, *ibid.*, 1969, **41**, 63R.
42. R. F. Gould, *Trace Inorganics in Water. Am. Chem. Soc.*, Washington, 1968.
43. M. J. Fishman and B. P. Robinson, *Anal. Chem.*, 1969, **41**, 323R.
44. H. B. Jacobs, *The Chemical Analysis of Air Pollutants*, Interscience, New York, 1960.
45. A. P. Altshuller, *Anal. Chem.*, 1969, **41**, 1R.
46. W. Leithe, *Allg. Prakt. Chem. Oesterr.*, 1969, **20**, (2), 36.
47. P. W. West, *Chemical Analysis of Inorganic Particulate Pollutants*, in *Air Pollution*, Vol. II, A. C. Stern, Ed., Academic Press, New York, 1970.
48. W. Strauss, Editor, *Air Pollution Control*, Wiley, New York, 1971.
49. G. Gottschalk, *Statistik in der quantitativen chemischen Analyse*, Enke-Verlag, Stuttgart, 1962.
50. K. Eckschlager, *Fehler bei der chemischen Analyse*, Geest und Portig, Leipzig, 1964; *Errors, Measurements and Results in Chemical Analysis*, Van Nostrand Reinhold, London, 1969.
51. K. Doerffel, *Statistik in der analytischen Chemie*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1966.
52. H. Schüller, *Mikrochim. Acta*, 1966, 742.
53. H. Kaiser and H. Specker, *Z. Anal. Chem.*, 1956, **149**, 46.
54. H. Kaiser, *ibid.*, 1965, **209**, 1.
55. *Idem*, *ibid.*, 1966, **216**, 80.
56. F. Feigl, *Mikrochemie*, 1923, **1**, 4.
57. R. Püschel, *Mikrochim. Acta*, 1968, 783.
58. J. Dokládalová and O. Stanková, *ibid.*, 1967, 857.

59. E. Broda and T. Schönfeld, *Radiochemische Methoden der Mikrochemie*, Springer-Verlag, Wien, 1955.
60. G. N. Bilimovich and I. P. Alimarin, *Zh. Analit. Khim.* 1957, **12**, 685; *J. Anal. Chem. USSR*, 1957, 12.
61. J. Tölgyessy, Š. Varga and V. Kriváň, *Nuclear Analytical Chemistry*, Vol. I. University Park Press, Baltimore, 1971; Vol. II in press.
62. E. Broda and T. Schönfeld, *Acta Chim. Acad. Sci. Hung.*, 1966, **50**, 49.
63. J. W. McMillan, *Analyst*, 1967, **92**, 539.
64. J. Růžička and J. Starý, *Substoichiometry in Radiochemical Analysis*, Pergamon, Oxford, 1968.
65. H. G. J. Bowen, *Chemical Applications of Radioisotopes*, Barnes and Noble, New York, 1969.
66. M. Braun, J. Tölgyessy and M. Kyrš, *Isotope Dilution Analysis*, Pergamon, Oxford, 1970.
67. A. Mizuike, in *Trace Analysis, Physical Methods*. G. H. Morrison, Wiley, New York, 1965.
68. R. Brown and P. G. T. Vossen, *Anal. Chem.*, 1970, **42**, 1820.
69. K. K. S. Pillay and C. C. Thomas, Jr., *J. Radioanal. Chem.*, 1971, **7**, 107.
70. H. Feuerstein, *Z. Anal. Chem.*, 1967, **232**, 196.
71. Technical Information Sheet, Vacuum/Atmospheres Corp., North Hollywood, Calif., USA.
72. F. A. Pohl, *Chem. Ing. Techn.*, 1958, **30**, 347.
73. F. A. Pohl and W. Bonsels, *Mikrochim. Acta*, 1960, 641.
74. P. R. Austin and St. W. Timmerman, *Design and Operation of Clean Rooms*, Business News Publishing Co., Detroit, 1965.
75. *Reine Räume und Werkplätze*, Richtlinien Juni 1966. Arbeitskeis Reine Räume e.V., Stuttgart (Schließfach 429).
76. Information Sheet, *Clean Rooms/Clean Benches*, South London Electric Equipment, Co. Ltd, London, S.E. 13.
77. G. Tölg, unpublished results.
78. K. Lieser, *Kerntechn.*, 1966, **8**, 74.
79. F. K. West, P. W. West and F. A. Iddings, *Anal. Chem.*, 1966, **38**, 1566.
80. R. G. Milkey, *ibid.*, 1954, **26**, 1800.
81. E. B. Butler and W. H. Johnston, *Science*, 1954, **120**, 543.
82. J. Dozer and M. Dole, *ibid.*, 1952, **115**, 93.
83. F. Kepák, *Chem. Rev.* 1971, **71**, 357.
84. G. G. Eichholz, A. E. Nagel and R. B. Hughes, *Anal. Chem.*, 1965, **37**, 863.
85. J. Murphy and J. P. Riley, *Anal. Chim. Acta*, 1956, **14**, 318.
86. G. Tölg, unpublished results.
87. T. Schönfeld and E. Broda, *Mikrochim. Acta*, 1951, **36/37**, 537.
88. D. E. Robertson, *Anal. Chim. Acta*, 1968, **42**, 533; *Anal. Chem.*, 1968, **40**, 1067.
89. I. J. E. Starik, *Grundlagen der Radiochemie*, p. 279. Akademie-Verlag, Berlin, 1963.
90. M. Yamada and S. Abe, *Bunseki Kagaku*, 1970, **19**, 843.
91. P. Gouverneur, H. C. E. van Leuven, R. Belcher and A. M. G. Macdonald, *Anal. Chim. Acta*, 1965, **33**, 360.
92. A. A. Benedetti-Pichler, *Mikrochim. Acta*, 1951, **36/37**, 38.
93. H. Böhm, K. G. Günther and W. Kuhl, *Z. Anal. Chem.*, 1965, **209**, 198.
94. G. Amsel and D. Samuel, *Anal. Chem.*, 1967, **39**, 1689.
95. K. Friedrich, *Sonderverfahren zur Gas-, Kohlenstoff- und Schwefelbestimmung*, in "*Spurenanalyse in hochschmelzenden Metallen*", Ed. H. J. Eckstein, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1970.
96. R. E. Thiers, in *Trace Analysis*, ed. J. H. Yoe and H. J. Koch, Wiley, New York, 1957.
97. L. S. Vasilevskaya, V. P. Muravenko and A. I. Kondrashina, *Zh. Analit. Khim.*, 1964, **20**, 540.
98. R. Delhez, *Chemist-Analyst*, 1960, **49**, 20.
99. G. Tölg, unpublished results.
100. G. Müller and G. Gnauck, *Reinste Gase*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1965.
101. I. P. Kharlamov, E. I. Dodin and A. D. Mansevich, *Zavodsh. lab.*, 1969, **35**, 3.
102. G. H. Morrison, *Preconcentration, Sampling, and Reagents*, in *Trace Characterization*, ed. W. W. Meinke and B. F. Schribner, Nat. Bur Std. Monograph 100, Washington, 1967.
103. G. Ehrlich, H. Engelhardt and A. Scholze, *Chem. Analit.* (*Warsaw*), 1966, **11**, 249.
104. T. Y. Toribara, C. P. Shields and L. Koval, *Talanta*, 1970, **17**, 1025.
105. E. Lassner, *Z. Anal. Chem.*, 1970, **252**, 380.
106. G. Tölg, unpublished results.
107. W. Ulmer and W. S. Tandler, *Laser Angew. Strahlentechn.*, 1970, **1**, 17.
108. K. H. Neumann and G. Matz, *Chem. Ing. Techn.*, 1955, **27**, 5.

109. R. Jaeckel, *Destillation und Sublimation im Fein- und Hochvakuum*, in *Methoden der Organischen Chemie*, ed. Houben-Weyl, I/1, 4th Ed., Thieme-Verlag, Stuttgart, 1958.
110. M. Behrens, H. Hahn and W. Neu, *Experientia*, 1966, **22**, 853.
111. J. Doležal, P. Povondra and Z. Šulcek, *Decomposition Techniques in Inorganic Analysis*, Iliffe, London, 1968.
112. T. T. Gorsuch, *The Destruction of Organic Matter*, Pergamon, Oxford, 1970.
113. K. H. Neeb, *Z. Anal. Chem.*, 1966, **221**, 200.
114. J. A. Stobart, *Analyst*, 1969, **94**, 1142.
115. W. Reichel and L. Acs, *Anal. Chem.*, 1969, **41**, 1886.
116. E. Scheubeck and O. Ernst, *Z. Anal. Chem.*, 1970, **249**, 370.
117. W. Geilmann and H. Bode, *ibid.*, 1951, **133**, 178.
118. W. Geilmann and R. Neeb, *ibid.*, 1957, **156**, 23.
119. K. S. Chung and F. E. Beamish, *Talanta*, 1968, **15**, 823.
120. K. Beyermann, *Z. Anal. Chem.*, 1964, **200**, 183.
121. R. Bock and D. Jacob, *ibid.*, 1964, **200**, 81.
122. J. Meyer, *ibid.*, 1965, **210**, 84.
123. G. V. Flyantikova, *Zavodsk. Lab.*, 1966, **32**, 529.
124. E. Fromm and H. Jehn, *Brit. J. Appl. Phys.*, 1965, **16**, 653.
125. G. Middleton and R. E. Stuckey, *Analyst*, 1953, **78**, 532.
126. E. Schulek and J. Laszlovsky, *Mikrochim. Acta*, 1960, 485.
127. O. Szakács and E. Schulek, *Ann. Univ. Sci. Budapest, Sect. Chim.*, 1964, **6**, 31.
128. P. O. Bethge, *Anal. Chim. Acta*, 1953, **8**, 397; 1954, **10**, 317.
129. W. Schöniger, *Z. Anal. Chem.*, 1961, **181**, 28.
130. A. M. G. MacDonald, *Analyst*, 1961, **86**, 3.
131. R. McGillivray and S. C. Woodger, *ibid.*, 1966, **91**, 611.
132. H. H. Taussky, A. Washington, E. Zubillaga and A. T. Milharat, *Microchem. J.*, 1966, **10**, 470.
133. B. Morsches and G. Tölg, *Z. Anal. Chem.*, 1966, **219**, 61.
134. W. Grote and H. Krekeler, *Angew. Chem.*, 1933, **46**, 106.
135. E. W. Seefield and J. W. Robinson, *Anal. Chim. Acta*, 1960, **23**, 301.
136. W. Radmacher and A. Hoverath, *Brennstoff, Chem.*, 1960, **41**, 304.
137. ASTM, Philadelphia, PA., *Standards on Petroleum Products and Lubricants*, Part 17, D 1266/645, p. 554, 1965.
138. Intern. Conf. Benzole Products, *Anal. Chem.*, 1964, **36**, 339.
139. C. E. Gleit and W. D. Holland, *ibid.*, 1962, **34**, 1454.
140. C. E. Gleit, *ibid.*, 1965, **37**, 314.
141. *Idem*, *Microchem. J.*, 1966, **10**, 7.
142. F. Dittel, *Z. Anal. Chem.*, 1967, **228**, 432.
143. G. Kaiser, P. Tschöpel and G. Tölg, *ibid.*, 1971, **253**, 177.
144. R. Wickbold, *Angew. Chem.*, 1952, **64**, 133.
145. F. Ehrenberger, S. Gorbach and K. Hommel, *Z. Anal. Chem.*, 1965, **210**, 349.
146. E. Kunkel, P. Gouverneur and F. Ehrenberger, *Proc. Collog.*, Heraeus-Schott Quarzschmelze GmbH, Hanau, BRD, 1966.
147. D. M. Coulson, *J. Gas Chromatog.*, 1966, **4**, 285.
148. R. L. Martin, *Anal. Chem.*, 1966, **38**, 1209.
149. P. Gouverneur, O. I. Snoek and M. Heeringa-Kommer, *Anal. Chim. Acta*, 1967, **39**, 413.
150. R. Belcher, *Talanta*, 1968, **15**, 357.
151. H. Weisz, *Mikrochim. Acta*, 1970, 1057.
152. G. F. Kirkbright, A. M. Smith, T. S. West and R. Wood, *Analyst*, 1969, **94**, 754.
153. G. F. Kirkbright, A. M. Smith and T. S. West, *ibid.*, 1967, **92**, 411.
154. F. Umland and G. Wünsch, *Z. Anal. Chem.*, 1965, **213**, 186.
155. V. A. Nazarenko and G. V. Flyantikova, *Zavodsk. Lab.*, 1958, **24**, 663.
156. G. Baudin, S. Lorrain and R. Platzer, *Trav. XXXV Congr. Intern. Chim. Ind., Varsovie*, 1965.
157. J. Minczewski, in *Trace Characterization*, ed. W. W. Meinke and B. F. Scribner, p. 385. Natl. Bur. Stds. Monograph 100, Washington, 1967.
158. J. R. De Voe and W. W. Meinke, *Anal. Chem.*, 1963, **35**, 2.
159. S. H. Omang, *Anal. Chim. Acta* 1971, **53**, 415.
160. E. Kunkel, *Z. Anal. Chem.* 1972, **258**, 337.
161. T. S. West, *Anal. Chim. Acta*, 1961, **25**, 405.
162. W. Maenhaut, F. Adams and J. Hoste, *J. Radioanal. Chem.*, 1970, **6**, 83.
163. J. Pijk and J. Hoste, *Anal. Chim. Acta*, 1962, **26**, 501.
164. E. Jackwerth and G. Graffmann, *Z. Anal. Chem.*, 1968, **241**, 96; 1970, **251**, 81.
165. E. Jackwerth, E. Döring and J. Lohmar, *ibid.*, 1971, **253**, 195.
166. L. Meites, *ibid.*, 1955, **27**, 416.

167. J. A. Page, J. A. Mayell and R. P. Graham, *Analyst*, 1962, **87**, 245.
168. R. Bock and K. G. Hackstein, *ibid.*, 1953, **138**, 339.
169. F. Lux, *Radiochim. Acta*, 1962, **1**, 20.
170. H. B. Mark, Jr. and F. J. Berlandi, *Anal. Chem.*, 1964, **36**, 2062.
171. G. Tölg, unpublished results.
172. J. Meyer, *Z. Anal. Chem.*, 1967, **231**, 241.
173. J. R. DeVoe, C. K. Kim and W. W. Meinke, *Talanta*, 1960, **3**, 298.
174. W. Angermann, in 2. *Intern. Symp. Reinststoffe in Wissenschaft und Technik*, *Dresden*, Akademie Verlag, Berlin, 1966.
175. V. I. Kuznetsov, in *Atomerergie; Tagung der Akademie der Wissenschaften der UdSSR, Abt. Chemie*, July 1955. Leipzig, 1957.
176. J. Kral, J. Jambor and L. Sommer, *Chem. Listy*, 1969, **63**, 1036.
177. F. Umland, *Theorie und praktische Anwendung von Komplexbildnern in der Analyse*, Verlag Chemie, Weinheim/Bergstraße, 1970.
178. A. K. De, S. M. Khopkar and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinhold, New York, 1970.
179. F. Umland and A. Janssen, *Fortschr. Chem. Forsch.*, 1966, **6**, 582.
180. Yu. A. Zolotov, *Ekstraktsiya vnutrikompleksykh soedinenii*, Izdat. Nauka, Moskau, 1968.
181. H. Freiser, *Anal. Chem.*, 1966, **38**, 131R; 1968, **40**, 522R.
182. G. H. Morrison and H. Freiser, *Anal. Chem.*, 1958, **30**, 632; 1960, **32**, 37R; 1962, **34**, 64R; 1964, **36**, 93R.
183. J. Starý, *The Solvent Extraction of Metal Chelates*, Pergamon, Oxford, 1964.
184. A. K. Babko and F. G. Zharovskii, *Zavodsk. Lab.*, 1962, **28**, 1287; *Ind. Lab. USSR.*, 1962, **28**, 1367.
185. Yu. A. Zolotov, *Zavodsk. Lab.*, 1962, **28**, 1404; *Ind. Lab. USSR.*, 1962, **28**, 1494.
186. A. K. De, *Separation of Heavy Metals*, Pergamon, Oxford, 1961.
187. L. Alders, *Liquid-Liquid Extraction*, 2nd Ed., Elsevier, Amsterdam, 1959.
188. G. Iwantscheff, *Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse*, Verlag Chemie, Weinheim/Bergstraße, 1958.
189. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry*, Wiley, New York 1957.
190. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon, Oxford, 1969.
191. R. Bock and A. Monnerjan, *Z. Anal. Chem.*, 1967, **226**, 29.
192. Y. Marcus, *Chem. Rev.*, 1963, **63**, 139.
193. A. K. De, *J. Sci. Ind. Res. India*, 1965, **24**, 82.
194. H. G. Döge, *Spurenanalyse in hochschmelzenden Metallen*, Deutscher Verlag für Grundstoffindustrie, Leipzig, 1970.
195. I. M. Grekova, *Ukr. Khim. Zh.*, 1969, **35**, 971.
196. W. Doll and H. Specker, *Z. Anal. Chem.*, 1958, **161**, 354.
197. G. H. Morrison and J. F. Cosgrove, *Symposium on Radiochemical Analysis*, 136th Meeting ACS, 1959.
198. P. C. van Erkelens, *Anal. Chim. Acta*, 1961, **25**, 129.
199. G. Tölg, *Z. Anal. Chem.*, 1962, **190**, 161.
200. R. A. Chalmers and D. M. Dick, *Anal. Chim. Acta*, 1965, **32**, 117.
201. S. J. Lyle and A. D. Shendrikar, *ibid.*, 1965, **32**, 575; 1966, **36**, 286.
202. H. Förster and K. Schwabe, *ibid.*, 1969, **45**, 511.
203. B. Morsches and G. Tölg, *Z. Anal. Chem.*, 1970, **250**, 81.
204. K. E. Schulte, G. Henke and K. S. Tjan, *ibid.*, 1970, **252**, 358.
205. R. O. Allen, L. A. Haskin, M. R. Anderson and O. Müller, *J. Radioanal. Chem.*, 1970, **6**, 115.
206. Z. Marczenko, K. Kasiura and M. Krasiejko, *Mikrochim. Acta*, 1969, 625.
207. W. Gebauhr, *Radiochim. Acta*, 1965, **4**, 191.
208. W. J. Ross, *Anal. Chem.*, 1964, **36**, 1114.
209. K. H. Neeb, H. Stöckert and W. Gebauhr, *Z. Anal. Chem.*, 1966, **219**, 69.
210. J. Korkisch, *Nature*, 1966, **210**, 626.
211. G. H. Morrison, J. T. Gerard, A. Travesi and R. Curie, *Anal. Chem.*, 1969, **41**, 1633.
212. E. Blasius, *Chromatographische Methoden in der analytischen und präparativen anorganischen Chemie unter besonderer Berücksichtigung der Ionenaustauscher*, in *Die chemische Analyse*, Bd. 46, Enke, Stuttgart, 1958.
213. M. Lederer, H. Michl, K. Schlögl and A. Siegel, *Anorganische Chromatographie und Elektrophorese*, in, *Handbuch der mikrochemischen Methoden.* Band 3, *Anorganische chromatographische Methoden*, Springer-Verlag, Wien, 1961.
214. O. Samuelson, *Ion Exchangers in Analytical Chemistry*, Wiley, New York, 1963.

215. K. Dorfner, *Ionenaustausch-Chromatographie*, Akademie-Verlag, Berlin, 1963.
216. *Idem*, *Ionenaustauscher: Eigenschaften und Anwendungen*, 3rd Ed., de Gruyter, Berlin, 1970.
217. J. Inczédy, *Analytische Anwendungen von Ionenaustauschern*, Akadémiai Kiadó, Budapest, 1964.
218. B. Trémillon, *Razdelenie na ionoobmennykh smolakh*, Izd, Mir., Moscow, 1967.
219. R. Kunin, *Anal. Chem.*, 1960, **32**, 67R; 1966, **38**, 176R.
220. R. Kunin and R. L. Gustafson *ibid.*, 1968, **40**, 136R.
221. W. Rieman and F. Walton, *Ion Exchange in Analytical Chemistry*, Pergamon, Oxford, 1970.
222. G. J. Moody and J. D. R. Thomas, *Analyst*, 1968, **93**, 557.
223. J. Korkisch, *Separation Science*, 1966, **1**, 159.
224. M. Lederer, *Anal. Chim. Acta*, 1955, **12**, 142.
225. *Idem*, *Bull. Soc. Chim. France*, 1966, 16.
226. K. A. Kraus and F. Nelson, *Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 1955, **7**, 113.
227. H. Green, *Talanta*, 1964, **11**, 1561.
228. B. Sansoni, *Neue chemische Arbeitsmethoden durch heterogene Reaktionen: Redoxaustauscher und numerometrische Titration.* Habilitationsschrift, Marburg, 1965.
229. R. Hering, *Chelatbildenede Ionenaustauscher*, Akademie-Verlag, Berlin, 1967.
230. A. Zlatkis, W. Bruening and E. Bayer, *Anal. Chem.*, 1969, **41**, 1692.
231. B. N. Laskorin, N. M. Smirnova and M. N. Gantman, *Ionenaustauschermembranen und ihre Anwendung*, Akademie-Verlag, Berlin, 1966.
232. G. H. Morrison and R. L. Rupp, *Anal. Chem.*, 1957, **29**, 892.
233. U. Eisner, J. M. Rottschaffer and F. J. Berlandi, *ibid.*, 1967, **39**, 1466.
234. F. Tera and G. H. Morrison, *ibid.*, 1966, **38**, 959.
235. G. Tölg, unpublished results.
236. W. J. Campbell, E. F. Spano and T. E. Green, *Anal. Chem.*, 1966, **38**, 987.
237. J. G. Bergmann, C. H. Ehrhardt and L. Granatelli, *ibid.*, 1967, **39**, 1258.
238. T. E. Green, S. L. Law and W. J. Campbell, *ibid.*, 1970, **42**, 1749.
239. C. W. Blount, W. R. Morgan and D. E. Leyden, *Anal. Chim. Acta*, 1971, **53**, 463.
240. H. Seiler, in E. Stahl, *Dünnschicht-Chromatographie*, Springer-Verlag, Berlin, 1967.
241. A. E. Sherwood, *Metallurgia*, 1969, **80**, 209.
242. F. W. H. M. Merkus, in *Progress in Separation and Purification*, Vol. III, ed, E. S. Perry and C. J. van Oss, Wiley, New York, 1970.
243. E. Cremer, Th. Kraus and H. Nau, *Z. Anal. Chem.*, 1969, **245**, 37.
244. G. Tölg, W. Lautenschläger and S. Pahlke, *ibid.*, in the press.
245. I. Schuphan, K. Ballschmiter and G. Tölg, *ibid.*, 1971 **255**, 116.
246. H. Weisz, *Microanalysis by the Ring Oven Technique*, 2nd Ed., Pergamon, Oxford, 1970.
247. K. N. Johri and H. C. Mehra, *Microchem. J.*, 1970, **15**, 642.
248. R. W. Fre and C. A. Stockton, *Mikrochim. Acta*, 1969, 1196.
249. V. Kriván, *Talanta*, 1969, **16**, 1513.
250. *Idem*, *Z. Anal. Chem.*, 1971, **253**, 192.
251. *Idem*, *VI Intern. Symp. Mikrochemie, Graz*, 1970, Verlag der Wiener Med. Akademie, 1970.
252. H. Meier, A. Ruckdeschel, E. Zimmerhackl, W. Albrecht, D. Boesche, W. Hecker, P. Menge, E. Unger and G. Zeitler, *Mikrochim. Acta*, 1969, 852.
253. R. E. Sievers, J. W. Connolly and W. D. Ross, *J. Gas Chromatog.*, 1967, **5**, 241.
254. H. Veenig, W. E. Bachman and D. M. Wilkinson, *ibid.*, 1967, **5**, 248.
255. W. D. Ross and R. E. Sievers, *Anal. Chem.*, 1969, **41**, 1109.
256. C. Genty, C. Houin, P. Malherbe and R. Scott, *ibid.*, 1971, **43**, 235.
257. R. Bock and H. J. Semmler, *Z. Anal. Chem.*, 1967, **230**, 161.
258. H. A. Rüssel, *ibid.*, 1970, **253**, 143.
259. W. D. Ross and R. E. Sievers, *Talanta*, 1968, **15**, 87.
260. J. K. Foreman, T. A. Gough and E. A. Walker, *Analyst*, 1970, **95**, 797.
261. G. Kaiser, E. Grallath, P. Tschöpel and G. Tölg, *Z. Anal. Chem.*, 1972, **259**, 257.
262. L. C. Hansen, W. G. Scribner, T. W. Gilbert and R. E. Sievers, *Anal. Chem.*, 1971, **43**, 349.
263. I. Schuphan, *Dissertation*, Univ. Mainz, BRD, 1970.
264. S. Nakashima and K. Toei, *Talanta*, 1968, **15**, 1475.
265. Ph. Larrat, *Chim. Anal. Paris*, 1969, **51**, 639.
266. K. Friedrich and E. Lassner, *J. Less-Common Metals*, 1967, **13**, 156.
267. R. K. Winge and V. A. Fassel, *Anal. Chem.*, 1969, **41**, 1606.
268. E. Lassner, *Mikrochim. Acta*, 1970, 820.
269. D. Jentsch and E. Otte, *Detektoren in der Gaschromatographie*, Akademische Verlagsgesellschaft, Frankfurt/M., 1970.
270. C. H. Hartmann and K. P. Dimick, *J. Gas Chromatog.*, 1966, **4**, 163.
271. H. P. Williams and J. D. Winefordner, *ibid.*, 1968, **6**, 11.

272. F. I. Scott and R. E. Rutherford, *Am. Lab.*, 1970, 43.
273. W. G. Pfann, *Zone Melting*, Wiley, New York, 1959.
274. E. E. Konovalov and S. I. Peyzulayev, *Trudy Kommis. po Analit. Khim.*, 1965, **15**, 375.
275. H. Kaneko, H. Kobayashi and K. Ueno, *Talanta*, 1967, **14**, 1403.
276. H. Kaneko, H. Kanagawa, N. Kobayashi and K. Ueno, *ibid.*, 1967, **14**, 1411.
277. Yu. A. Zolotov and N. M. Kuz'mun, *Ekstraktsionnoe kontsentrirovanie*, Izd. Khimia Moscow, 1971.
278. K. Beyermann, *Z. Anal. Chem.*, 1961, **183**, 91.
279. H. Irving and I. I. Cox, *Analyst*, 1958, **83**, 526.
280. C. A. Goetz and F. J. Debbrecht, *Anal. Chem.*, 1955, **27**, 1972.
281. F. W. Chapman, G. G. Marvin and S. Y. Tyree, *ibid.*, 1949, **21**, 700.
282. K. Beyermann, *Z. Anal. Chem.*, 1962, **190**, 4.
283. H. Stegemann, *ibid.*, 1957, **154**, 267.
284. M. Tatsumoto, *Anal. chem.*, 1969, **41**, 2088.
285. H. G. Döge, in *Spurenanalyse in hochschmelzenden Metallen*, ed. H. J. Eckstein, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1970.
286. L. S. Vasilevskaya, V. P. Muravenko and A. I. Kondrashima, *Zh. Analit. Khim.*, 1965, **20**, 540.
287. E. W. Harpham, *Metallurgia*, 1955, **52**, 45.
288. E. M. Dodson, *Anal. Chem.*, 1962, **34**, 966.
289. R. Bock and A. Herrmann, *Z. Anal. Chem.*, 1969, **248**, 180.
290. P. G. Jeffery, *Analyst*, 1957, **82**, 67.
291. W. R. Schoeller, *ibid.*, 1931, **56**, 305.
292. K. Beyermann, *Z. Anal. Chem.*, 1963, **194**, 1.
293. B. Bernas, *Anal. Chem.* 1968 **40**, 1682.
294. M. M. Smith and C. James, *J. Am. Chem. Soc.*, 1920, **42**, 1764.
295. G. J. Petretic, *Anal. Chem.*, 1951, **23**, 1183.
296. W. E. Clarke, B.C.I.R.A. Journal., 1961, **9**, 185.
297. E. W. Harpham, *Metallurgia*, 1955, **52**, 93.
298. H. J. M. Bowen, *Anal. Chem.*, 1968, **40**, 969.
299. K. Fukami, *Min. Metallurg. Inst. Japan*, 1960, **76**, 35.
300. K. C. Agrawal and F. E. Beamish, *Talanta*, 1964, **11**, 1449.
301. R. Thiers, W. Graydon and F. E. Beamish, *Anal. Chem.*, 1948, **20**, 831.
302. W. J. Allan, and F. E. Beamish, *ibid.*, 1952, **24**, 1569.
303. G. H. Faye and W. R. Imman, *ibid.*, 1957, **31**, 1072.
304. C. O. Ingamells, *Talanta*, 1964, **11**, 665.
305. J. C. van Loon and C. M. Parissis, *Analyst*, 1969, **94**, 1058.
306. V. S. Biskupsky, *Anal. Chim. Acta*, 1965, **33**, 333.
307. A. M. Bond and D. R. Canterford, *Anal. Chem.*, 1971, **43**, 134.
308. W. Geilmann and R. Neeb, *Angew. Chem.*, 1955, **67**, 26.
309. *Idem*, *Z. Anal. Chem.*, 1959, **165**, 251.
310. W. Geilmann, *ibid.*, 1958, **160**, 410.
311. W. Geilmann and H. Hepp, *ibid.*, 1964, **200**, 241.
312. Geilmann and A. de Alvaro Estebaranz; *ibid.*, 1962, **190**, 60.
313. W. Gebauhr and A. Spang, *ibid.*, 1960, **175**, 175.
314. K. H. Neeb, *ibid.*, 1963, **194**, 255.
315. K. Beyermann, *ibid.*, 1961, **183**, 91.
316. E. Lassner, *VI. Intern Symp. Mikrochem., Graz*, 1970. Preprints Vol. B, p. 157. Verlag Wiener Med. Akad., 1970.
317. E. Lassner and R. Püschel, *Monatsh. Chem.*, 1964, **95**, 812.
318. J. E. Mathers, G. V. Potter and N. W. Shearer, *Anal. Chem.*, 1962, **30**, 1412.
319. J. Inczédy, *Periodica Polytech.*, 1970, **14**, 149.
320. P. Jannasch and R. Seiske, *J. Chem. Soc.*, 1918, **114**, 460.
321. P. Janasch and O. Laubi, *J. Prakt. Chem.*, 1918, **97**, 150.
322. K. G. Isaeva and L. G. Zhuravlev, *Tr. Inst. Mineralog. Geokhim. i Krystalokhim. Redkikh Elementov, Akad. Nauk SSSR*, 1959, p. 278; *Anal. Abstr.*, 1960, **7**, 3183.
323. E. G. Berns and P. W. Van der Zwann *Anal. Chim. Acta*, 1972 **59**, 293.
324. L. Morgan, *Analyst*, 1964, **89**, 621.
325. V. R. Wiederkehr and G. W. Goward, *Anal. Chem.*, 1959, **31**, 2102.
326. A. R. Gahler and G. Porter, *ibid.*, 1957, **29**, 298.
327. W. Maenhaut, F. Adams and J. Hoste, *J. Radioanal. Chem.*, 1970, **6**, 83.
328. M. M. Piryutko, *Zavodsk. Lab.*, 1963, **29**, 1179.

329. K. I. Zil'bershtein, M. M. Piryutko, O. N. Nikitina, Yu. F. Federov and A. V. Nenarokov, *ibid.*, 1963, **29**, 1266.
330. D. M. Shvarts, *ibid.*, 1962, **28**, 684.
331. Analytical Methods Committee, *Analyst*, 1967, **92**, 403
332. J. L. Down and T. T. Gorsuch, *ibid.*, 1967, **92**, 398.
333. G. F. Smith, *Talanta*, 1964, **11**, 633.
334. *Idem*, *ibid.*, 1968, **15**, 489.
335. G. R. Doshi, C. Sreekumaran, C. D. Mulay and B. Patel, *Curr. Sci.*, 1969, **38**, 206; *Anal. Abstr.*, 1970, **19**, 1574.
336. T. T. Gorsuch, *Analyst*, 1959, **84**, 135.
337. B. Sansoni and W. Kracke, *Z. Anal. Chem.*, 1968, **243**, 209.
338. B. Bernas, Atomic Absorption Newsl., 1970, **9**, 52.
339. L. Kotz, G. Kaiser, P. Tschöpel and G. Tölg, *Z. Anal. Chem.* 1972, **260**, in press.
340. R. Bock and P. Tschöpel, *ibid.*, 1969, **246**, 81.
341. H. Buss, H. W. Kohlschütter and S. Miedtank, *ibid.*, 1960, **178**, 1.
342. K. E. Burke, *Anal. Chem.* 1970, **42**, 1536.
343. H. G. Döge and H. Grosse-Ruyken, *Isotopehpraxis*, 1968, **4**, 262.
344. K. H. Neeb and W. Gebauhr, *Z. Anal. Chem.*, 1958, **162**, 167.
345. H. A. Rüssel and G. Tölg, *Fortschr. Chem. Forsch.*, in press.
346. B. I. Anvaer and J. S. Drǔgov, *Zh. Analit. Khim.*, 1971, **26**, 1180.
347. A. Mizuike, K. Fukuda and Y. Ochiai, *Talanta*, 1972, **19**, 527.
348. R. Bock, Aufschlußmethoden der anorjanischen und organischen Chemie, Verlag Chemie, Weinheim/Bergstraße, 1972.

Talanta, 1972. Vol. 19, pp. 1523 to 1547. Pergamon Press. Printed in Northern Ireland

TALANTA REVIEW*

DETERMINATION OF WATER

CLIFFORD HARRIS†
88 Charlton Road, Keynsham, Nr. Bristol, U.K.

(*Received* 15 *October* 1971. *Accepted* 7 *May* 1972)

Summary—The complexity of the subject and the problems involved in the estimation of water in the many materials required to be tested are explained. The various methods available are classified, their techniques summarized, and their applications and limitations indicated. In many materials the determination of absolute moisture is impossible and a compromise must be accepted. Trade and industry require rapid results for many processes and products, and optical or electronic methods are increasingly used in conjunction with reference methods. For official purposes the method of determination must be agreed and stated in detail. More progress in international standardization is very desirable.

A KNOWLEDGE of the water or moisture content of a substance is a matter of universal importance because it is required not only by research workers but by various authorities and firms processing chemicals, foods and other materials. The water content will often determine the nature, consistency and keeping quality or storage properties of a material and will play a large part in the economics of a process, water being the cheapest raw material other than air.

The estimation of water is usually required as part of a general analysis and the water may vary from a trace amount to a quantity approaching 100%; the substance to be tested may be solid, liquid or gas. The method used will depend on the following factors.

1. Availability of the sample and its physical state.
2. Stability of the sample to heat.
3. Presence of volatile material other than water.
4. Retention of water by sample.
5. Amount of water present.
6. Time available and frequency of testing.
7. Cost of estimation.
8. Accuracy required.

It is impossible to determine the absolute water content of the majority of composite materials. Many foods and other organic materials begin to decompose towards the end of a heat-drying process and there may be a slow continuous loss of weight due to substances other than water. Quantity, time and temperature have to be fixed to give a result close to the true water content. Such a result is empirical but usually adequate for the purpose required. The difficulty lies in obtaining agreement between different laboratories, and authorities, and because of this there are many "official

---

* For reprints of this review see Publisher's announcement near the end of the issue.

† Formerly Chief Analyst, J. S. Fry & Sons, Bristol (Cadbury Bros. Ltd.)

methods" for specified materials (see section on Reference Methods). These methods and associated apparatus are published in detail and if closely followed will give reproducible results. There is a very extensive literature dealing with water or moisture determination. A symposium was held by the American Chemical Society in 1951,[1] and an International Symposium on humidity and moisture was held in Washington D.C. in 1963.[2] Geary (British Scientific Instrument Research Association) reviewed methods for determining moisture in solids in 1956 and again in 1970.[3] Many other reviews deal only with particular materials, *e.g.*, honey.[4]

The present review places emphasis on the practical rather than the theoretical side. References to instruments illustrate principles or indicate types available and imply no special recommendations, being indicative only of the author's experience.

SAMPLING

Results are meaningless if samples are not uniform and representative. Recognized methods of mixing and bulking may be followed but moisture may be lost by evaporation, or gained if the material is hygroscopic. Official tests will give some guidance. Problems occur when solid materials have to be milled or pulverized. Precautions can be taken or a correction made for moisture gain or loss, as the result of trials. Enclosed mixers for blending and grinding are used which utilize high-speed multi-bladed stainless-steel rotary cutters. The general capacity is about 1 litre but much larger ball mills are available. Micro hammer-mills will deal effectively with small samples.[5] Other apparatus can combine grinding with extraction with a solvent such as methanol (see section on titrimetric methods).

Closed containers are required to hold the samples before testing. Liquids are easier to deal with but in sampling them care must be taken to distribute and include sediment or crystals if it is desired to know the water content of the whole. This may be troublesome, for example, with bulk containers of partly crystallized honey or highly concentrated syrups.

The water content of a substance is usually given as a direct percentage of the material as sampled and tested but in some trades the water may be required for practical considerations as a percentage relative to the weight of the dry substance, for example, textiles and wood.

Water retention

Water in solid materials may be held in various ways. It may be present as water of crystallization, *e.g.*, lactose hydrate in milk products. Many pure chemicals exist as hydrates. Water can be held chemically bound in association with protein as in plant cells or organic matter, or absorbed as in fibres; it can exist in pores or as "free" or surface moisture. These are some factors which will influence the choice of method of estimation. In rocks and minerals, water may be loosely bound "interstitial" water, removable at temperatures little above 100°, or chemically bound "constitutional" water, which may be retained in part even at temperatures up to 1000°. Rock analysis is dealt with in the *Appendix*.

CLASSIFICATION OF METHODS

The diversity and overlapping of parts of methods make scientific classification difficult. Some are more or less direct methods; others are indirect. Some require other procedures for calibration.

Classification may be based on physical, chemical, electrical and radioisotope methods, but the following is used in this survey of the more usual methods.

- Drying methods (range of estimation approx. 0–100%)
  - By desiccant
  - By freeze drying
  - By heat at atmospheric pressure
  - By heat under reduced pressure
- Distillation with immiscible liquid—Dean and Stark (range of estimation 0–100% approx. but lower accuracy for water > 20%)
- Titrimetric—Karl Fischer (range of estimation usually 0–15% but can be extended to 100%)
- Optical
  - Refractometric (range of estimation approx. 15–100% for specified solutions)
  - Infrared absorption (range of estimation approx. 0–100%)
- Vapour pressure
  - Equilibrium relative humidity (E.R.H.) and relative humidity (R.H.) (limited ranges of estimation for specified materials)
- Electronic
  - Conductance and capacitance (limited ranges of estimation)
  - Microwave attenuation (range of estimation approx. 0–100%, more usually 5–35%)
  - Nuclear magnetic resonance (NMR) (range of estimation approx. 0–100%)
  - Nuclear radiation (range of estimation approx. 0–100%)
- Miscellaneous
  - Apparatus and methods for specified purposes (various ranges of estimation)

Drying methods

These depend on recording the loss of weight of a solid or liquid after drying or on the gain in weight of a desiccant (gases).

By desiccants. These are among the oldest methods. Drying is carried out, at room temperature for heat-sensitive materials, in a desiccator over concentrated sulphuric acid, sometimes with a supported upper layer of sodium hydroxide flakes, and with or without the application of vacuum. Anhydrous phosphorus pentoxide, calcium sulphate or calcium oxide may also be used, as applicable. Drying is very slow with some materials and the method is not of general use except for isolated investigations of heat-sensitive material.

Techniques are also used whereby dry air or nitrogen is passed over the sample and through a desiccant in a weighed U-tube and the gain in weight is related to water. Heat is used where possible. This procedure may be useful for large samples holding but little water as the U-tube can be weighed very accurately. Gases are tested in like manner if they themselves have no reaction with the desiccant.

Freeze-drying. Drying from the frozen state is often the only safe method of removing water from heat-labile biological substances without producing undesirable chemical changes. Tappel has described a laboratory freeze-drying apparatus.[6] Water is removed under high vacuum from the frozen test substance by sublimation, the receiver being cooled by "dry ice"/acetone or liquid nitrogen (lyophilization). Cell walls are broken down and the water released. The final traces can often be removed by other methods of drying without decomposing the material.

By heat at atmospheric pressure. These methods have the widest application for many solids and liquids, and require relatively cheap apparatus. The results are often recorded as "loss at 100°." Willits[1] reviewed the basic problems of oven-drying, in 1951. The suitably prepared sample is spread over the bottom of a "moisture bottle"—a flat-bottomed shallow dish with ground-glass cover which is used to close the dish before and after the drying process to avoid moisture change during weighing. It is essential that the bottom surface be flat for a drying procedure dependent on heat, so that the heat gain is uniform when a number of vessels are used.

For many purposes flat-bottomed seamless dishes with close-fitting slip-on lids made of nickel, stainless steel or aluminium may be used. The diameter is usually between 4 and 8 cm. Official methods always quote dimensions. Modern aperiodic balances reduce weighing time and minimize moisture pick-up after drying. For batch-testing the lids and dishes are numbered. Some workers stand the moisture dish inside its inverted lid in the oven and if the bottom of the dish and the lid give a flush fit with each other and the shelf there is usually no influence on the result, but official procedure is to partly remove the lid or lean it adjacent to the dish in the oven. A British Standard Method[7] for liquid milk is exceptional in requiring the bottom of the dish to be insulated from the shelf. After drying, the dish is closed with its lid and allowed to cool to room temperature in an anhydrous calcium chloride (or calcium oxide or sulphate or silica gel) desiccator before reweighing. Half-an-hour of cooling may be required, depending on the number of dishes, but the minimum time should be allowed.

About 5 g is taken for a test as this amount gives the required accuracy when using a "milligram" balance. Limitations on weight may be set by bulkiness, or water-retention properties. Official tests will always state the weight, which may be 1–10 g or even much more.

Reproducibility is better than 0·1 % for many materials, which is satisfactory for most purposes, but refined sugar for example will have a water content as low as 0·02 % and results are required to the second decimal place. Weighing then must be more accurate.

The traditional oven had a jacket of boiling water but this type has largely been displaced by insulated ovens with thermostatically controlled electric elements in the base and sometimes the sides, with a fan for circulating the air so that the temperature anywhere on the shelves remains practically constant. A British Standard[8] sets out conditions for laboratory drying ovens and pays particular attention to temperature variation and ventilation.

Drying time may vary from 2 hr to overnight or longer—this being subject to a knowledge of the properties of the test materials. Many official tests require redrying to "constant weight"—often defined as further loss not exceeding 5 mg. Some stipulate a further loss not exceeding 2 mg (0·5 mg for milk products). This provides a check on the ventilation and possible overloading of the oven and is always necessary when testing new substances.

Drying at 100° at atmospheric pressure is not suitable for many substances with a glue-like or syrupy nature, where water-retention properties are strong and where a skin or crust can form. The difficulty can be overcome in some cases by dispersal as a solution on weighed, dried and purified pumice granules or sand in the moisture vessel. The British Standard Method for liquid milk stipulates predrying for 30 min on a steam-bath before final drying in an oven at 100°; evaporated and sweetened condensed milk (weighed) is mixed first with water by means of a glass rod and then with dry sand (both weighed) in a moisture dish, the mixture being predried with stirring on a steam-bath before final drying at 98—100°.[9] The object is to produce an aerated mixture for the final drying and not a hard cake.

Temperatures above 100° are also used. The British Standard (B.S.) for milk powder requires 102–103°.[10] The B.S. for gelatine is 105° for 18 hr after a predrying process to produce a uniform film, by dissolving 1 g in water in the moisture dish and drying on a steam-bath.[11]

There may be shelf-to-shelf variations with individual ovens and it is advisable to make preliminary multiple tests with a uniform sample, placing the moisture vessels in various parts of the oven. Even when an oven with a fan is used, it is possible for results to differ by as much as 0·6% in testing milk powder at a nominal 102°. Temperatures tend to be higher at the sides of the ovens and lower near the doors.

There are several variations of the simple oven. *The Imperial Tobacco Co. Oven*[12] was designed to handle very large numbers of tobacco samples. The steam-jacketed oven is suitable for any material to be tested for "loss at 100°." The steam is condensed and the condensate returned to the electric boiler in the base of the apparatus. Air is aspirated through the central support in the circular chamber and across each shelf before leaving the exit tube. The test-samples are carried on a 10-tier circular rack within the heated jacket and can be removed from the top by lifting back the hinged head of the oven. Heat-gain is constant as all vessels are exposed to the same degree of conduction and radiation and the oven meets the requirements of a uniform temperature of 100° with adequate removal of moist air. For many substances 4 hr drying is sufficient and 80 test-samples can be accommodated.

Moisture in tobacco is legally defined as the loss in weight when tobacco is dried at 212°F and the standard is fixed by the U.K. 1952 Customs and Excise Act as 14% for calculating refund of duty. The Laboratory of the Government Chemist makes 150,000 tests per annum, using *Air Flow Ovens*[13] based closely on the principles of the original I.T.C. oven. The test-samples are dried for 17 hr with an air-flow of 12·5 l./min. Tobacco is bulky and for this reason perforated lids are used which are left on the moisture vessels, even throughout the drying period, to avoid spillage. On removal from the ovens the vessels are not placed in desiccators to cool but are stacked one above the other in special racks so that the holes are covered, the top vessel being empty.

The *Brabender Oven*[14] is a combined oven and balance. Each dish must be exactly the same in weight but there is the advantage that no time is lost in waiting for the dishes to cool in the desiccator. The oven is provided with forced hot-air circulation. A circular support carries 10 aluminium dishes for simultaneous drying and by turning a central knob each dish can be brought over the balance in turn for weighing *in situ* without interrupting the drying, which may be prolonged for a further period if desired. Some workers use the oven at 105° for 1 hr, finding that this gives reasonable agreement with reference methods for many common commodities. Bauer[15] determined the optimum temperature and time for various pharmaceutical products for comparison of results with those given by vacuum drying and the Karl Fischer technique.

The *Mytron Oven*[16] is similar in principle to the Brabender oven but the apparatus is of more recent development. The volume of predried air blown into the drying chamber can be regulated and during the drying process the disc holding the 10 moisture vessels is rotated to give uniform conditions. A switch coupled to the balance controls this rotation and a safety device ensures there is no movement of the disc during weighing. Ten-gram samples are normally tested and the results for loss on drying are projected onto a screen. Thermostatic control is obtained over the range 50–150°. A reproducibility of ±0·1 % is claimed.

The *Carter Simon Oven*[17] is relatively simple and useful for some products which have to be tested regularly throughout the day for process control. It holds three test vessels in line and a freshly weighed one is pushed in through a flap at 5-min intervals. As one goes in it ejects another through the opposite flap so that each spends 15 min within the oven, which is ventilated with preheated air. Such rapid drying demands a high temperature and results are merely empirical. The thermostat must be set for each material, to obtain results as close as possible to those given by a suitable reference method (examples from the author's laboratory are: starch 5 g at 155°, wafer biscuit 2 g at 120°). After the initial delay for cooling, results follow at 5-min intervals—time enough for weighing and calculating results.

Radiant Lamp (*Infrared*) *Moisture Testers* are usually based on a sample being on a balance pan and heated from above by means of an infrared lamp. They usually have the advantage possessed by the Brabender oven, of following the weight loss without interrupting the drying process, which enables time and heat to be standardized to give "moistures" values before loss by decomposition increases unduly. They are useful for routine testing of materials which give up their moisture readily, but the heat of the lamp can be affected by aging and voltage variation and there is no thermostat to correct for this.

Some testers incorporate a voltage controller and this is used to adjust the lamp intensity, thus avoiding adjustment of the lamp height. Analysis in random order of samples with widely-differing water content introduces errors, as low-moisture samples will be heated for longer than it takes to drive the water off, whereas high-moisture samples may not lose all their water in the fixed time interval, and so the calibration for a fixed lamp-height (or voltage) and time holds only for a particular range of moisture contents.

Results obtained by infrared drying are also affected by the thermal history of the apparatus and may become progressively higher as determinations progress throughout the day. Thermal equilibrium is not reached immediately the lamp is switched off, thus starting temperatures are variable unless a fixed sequence is adopted. Nevertheless if due regard is given to these factors when calibrating, moisture testers using infrared lamps can serve a very useful industrial purpose.

Recording Balances are designed so that the sample can be hung from the rear pan of a precision balance of the aperiodic type and be heated in any suitable oven, the weight-loss *vs.* time curve being recorded on a chart for up to several days if required. Rate of loss of free water can be followed and steps on the chart will show the existence of hydrates and transition points—useful for preliminary investigation. Double pen recorders for both weight and temperature are available.[18]

Some tests on hydrates with recording differential thermogravimetric balances have been described by Waters.[19]

By heat under vacuum. As indicated above, many substances will not yield up all their water under the simple application of heat, owing to their strong water-retention properties. During the drying process at atmospheric pressure the vapour pressure of the material decreases and the rate of drying is greatly retarded. Complications are introduced by crust formation producing low results, with decomposition working in the opposite direction to give high results. Fructose (laevulose) will decompose at 100° to give high moisture results for materials containing it, such as honey and invert sugar. Drying under vacuum at a lower temperature can overcome some of the problems if significant amounts of volatiles are not present, and the method is usually quicker. Vacuum drying is now included with officially recognized tests for some materials. Commercial laboratories use vacuum ovens because of their wide general application and the speed with which results can be obtained with otherwise slow-drying samples. Ovens can be obtained either with heated shelves or heated jackets.[20]

It is not easy to obtain an accurate knowledge of the temperature under vacuum as there is a drop in the observed reading, due to slight expansion of the thermometer bulb. A sleeve overcomes this but the temperature indicated is lower than that of the test material. As part of the preliminary testing the thermometer bulb should be placed in the test material in the dish in contact with the heated shelf. Electrical thermistors are best for checking. Under the shelf is a sliding tray which may contain silica gel desiccant. Vacuum is applied by means of an external pump. An oven may hold 10–15 dishes, depending on their size. One pump can exhaust and maintain several ovens under vacuum.[21] Most mechanical ones are fitted with oil traps and non-return valves and some with phosphorus pentoxide moisture-traps. Generally the water evolved by samples under test is not sufficient to cause trouble with modern rotary pumps and the degree of vacuum need not be high. It is best to standardize on a degree of vacuum—some workers prefer 20 mmHg, others obtain more consistent results with pressures of 5 mmHg. A Cartesian-type manostat is used for this purpose in the vacuum line between the pump and the oven(s). Once preset it will allow the pump to exhaust down to the desired pressure and not lower. An accurate barometrically-compensated dial manometer reading directly 0–100 mmHg is required.

The door of the oven is clamped, and made air-tight by a rubber gasket which must be maintained in good condition. Some leak will nearly always be present and this is not a matter for concern provided the pump can cope, as an air-bleed is desirable and some workers introduce one to make sure that there is some flow through the oven. Some official tests require a "bleed" of dry air.

The drying temperature chosen is usually between 60° and 80°; 70° is preferred by some as giving consistent results in a reasonable time without decomposition. Two hr drying may be satisfactory but 4 hr is often used in a standardized procedure with a mixed lot of test-materials. Also for convenience, overnight drying may be used without results being materially different. When the vacuum is first applied, care must be taken that materials do not spatter or foam, and when air is finally admitted it is usual to proceed slowly to prevent powders being blown about. Once started, the vacuum must not be "broken "or aerated materials may collapse and lose the open texture so necessary for the free evaporation of water.

Some materials need pretreatment for successful results to be obtained. Viscous materials such as jams, honey, caramel, nougatine, boiled sweets, require dispersion as a solution on dried, purified sand or 4–8 mesh pumice for results consistent to the first decimal place to be obtained. There are various techniques employed, based on weighing the sample into a moisture dish containing a short glass stirring rod and previously dried (ignited) sand or pumice. Hot water is added and the weighed test substance slowly dissolved for dispersion on the sand or pumice, the stirrer being left in the dish. The mixture is partially predried on a steam-bath with occasional stirring, before final drying under vacuum. A hard skin must not be allowed to form, neither should the mixture be so moist as to spatter under vacuum. Results of multiple tests on the same sample will show if the correct technique is being used.

The *Infrared Vacuum Oven*[22] is useful where single results are required quickly under factory conditions, provided vibration is not excessive, as a test can be completed in about 10 min. The apparatus uses a variable-temperature infrared lamp and a single-pan torsion balance, both enclosed in a chamber which can be evacuated. A 5-g sample is spread on a foil disc and placed on the pan after removal of a counter weight. Very viscous materials may require spreading with a polytetrafluoroethylene roller, followed by re-adjustment of weight. The cover of the apparatus, usually preheated, is closed and clamped and the vacuum applied. The balance beam is restored to its original null position as indicated by an index pointer, by rotating a drum or wheel calibrated directly in percentage moisture. This can be done at the end of an agreed standard time or while drying continues and so its progress followed. The test is an empirical one as with all infrared drying methods, but conditions can be chosen to give results close to "standard" ones.

As practical examples, carbon black heated on heat scale No. 5 attains 140° in 8 min, and drying is complete; application of 80 V for 20 min at 10 mmHg will give a satisfactory result with nougatine. Caramel spatters, however, and this method is unsuitable. For uniform testing it is best to use a constant-voltage transformer if there are mains variations.

Distillation methods—entrainment or azeotropic distillation

The procedure is to heat the sample in a flask with a liquid immiscible with water so that water vapour is carried into a reflux condenser with vapour from the boiling solvent. The condensate is collected in a graduated tube where the water separates and the volume can be read. The Dean and Stark apparatus[23] is much used with immiscible liquids lighter than water, such as heptane, toluene or xylene (b.p. 98°, 111°, and 140° respectively). The entrainment liquid overflows from the water trap and returns to the original flask while boiling continues. Usually less than 1 hr is sufficient to transfer all the water from the test-sample to the graduated receiver.

With 100-g samples results can be read to a satisfactory degree of accuracy, depending on the water content and correct selection of receiver, but 50 g and often less may taken for test. Some types of apparatus have a draw-off tap for the moisture trap and this extends the range for testing materials with high water-content; emptying and cleaning the apparatus at the end of each test is then not necessary.

The method is suitable for butter, petroleum, oils and fatty materials in general, but not for those which do not disperse in the boiling liquid. Syrups and sugary materials which settle and stick on the bottom of the flask will burn. Fetzer[1] recommended that such materials should first be dispersed on dry diatomaceous earth. Anti-bumping aids, *e.g.*, dry asbestos, can also be used.

The distillation method has the advantage that the water can be seen and the separation observed throughout the test. Volatiles soluble in the water-immiscible solvent do not interfere. The condenser and receiver must be kept very clean to avoid droplets of water adhering to the glass surfaces. It is possible to detach droplets from the condenser and make them join with the water in the graduated part of the receiver with a glass rod or by spray tube at the end of the test. Barr and Yarwood[24] recommend baking silicone oil on the apparatus before use. A B.S.[25] gives details of the Dean and Stark apparatus. Immiscible liquids heavier than water, such as carbon tetrachloride, perchloroethylene and tetrachloroethane, may also be used, the upper part of the receiver being graduated. Excess of entrainment liquid flows from the bottom part back to the original flask. These solvents have the advantage of being non-inflammable. The most suitable liquid will depend on the material to be tested. Fetzer[1] preferred toluene, but benzene (b.p. 80°) if the material was heat-sensitive. Meredith *et al.*[26] compared the distillation method with the Karl Fischer and vacuum methods for cereal grains and by-products and found toluene very satisfactory. Harel and Talmi[27] reported that xylene removed free water and water of crystallization from gypsum, but benzene did not, and thus suggested a means for examining hydrates.

The determination of water down to 0·01 ml in some plastic materials by use of xylene and downward condensation of the vapours was described by Alsop and Wadsworth.[28] The method avoids droplets of water remaining in the condenser.

Titrimetric methods—Karl Fischer titration

The titration method published by Fischer[29] in 1935 has been widely adopted and is in use in many laboratories. It is convenient and rapid for the accurate estimation of small amounts of water (up to 100 mg) where there is no interference with the reagent by other chemical compounds. The Karl Fischer (K.F.) reagent consists of iodine and sulphur dioxide in pyridine–methanol solution and it reacts with water according to the equations:[30]

$$SO_2 + I_2 + H_2O + 3\,C_5H_5N \rightarrow 2\,C_5H_5N{\cdot}HI + C_5H_5NSO_3 \qquad (1)$$

$$C_5H_5NSO_3 + CH_3OH \rightarrow C_5H_5NH{\cdot}SO_4{\cdot}CH_3 \qquad (2)$$

Only reaction (1) involves water; (2) completes reaction of the intermediate pyridine–sulphur trioxide complex. One molecule of iodine is theoretically equivalent to one molecule of water but in practice the K.F. reagent must be standardized against a known amount of water. Excess of iodine is shown by the colour but the end-point is nearly always obtained electrometrically by the "dead-stop" technique using a microammeter which indicates a sudden increase in current when the platinum electrodes are depolarized. Various types of apparatus have been designed to do this and to make the titration semi-automatic.[31]

The K.F. reagent is hygroscopic and very sensitive to moisture, and the reagents, solvents, burettes, titration vessel *etc.*, must be guarded by silica gel tubes (containing a water-sensitive indicator to show when their desiccant capacity is exhausted). Other ancillary glass apparatus is dried at 100° before use.

Anhydrous methanol is used as a sample solvent but a 4:1 mixture of methanol and pyridine is better for many materials. Some workers use other mixtures such as 7:3 methanol–formamide, or 3:2:1 formamide–chloroform–methanol which are preferred for dissolving or dispersing sugar products, but formamide tends to give high blanks (author's laboratory). The K.F. reagent has a titre equivalent to approx. 5 mg of water per ml and a methanol solution of water with this concentration is used as a means of back-titrating to give a sharper end-point. A typical apparatus has 2 burettes connected to an enclosed titration vessel fitted with a magnetic stirrer. The solvent mixture added to this vessel is titrated to the null-point for each series of tests. The powdered sample is added through a side tube and titrated after allowing time for dispersion or dissolution to take place. This may take 5 min, but generally a titration is completed in less than 10 min, and the method is a rapid one providing all is ready, but it is essentially a laboratory method and not suitable for use under factory or field conditions.

The K.F. reagent must be standardized daily, usually with distilled water added to the titration vessel from an "Agla" or other micrometer-syringe. Hydrates such as disodium tartrate dihydrate and sodium acetate trihydrate are also employed for standardization, 0·2–0·6 g being added to the solvent in the titration vessel and titrated with the K.F. reagent. The theoretical water content of these hydrates must be checked by drying at an appropriate temperature (*e.g.*, 150° for the tartrate, 130° for the corresponding acetate).

The methanol can be purchased specially dried. A B.S. for the Karl Fischer method of water estimation gives details of apparatus and reagents.[32]

Some materials cannot be dispersed to give up all their water in the titration vessel and it is best to give a preliminary treatment with a solvent mixture in a flask with heating, or boiling under reflux if necessary, and then transfer the mixture or an aliquot to the titration vessel. To give an example, taking caramel as a "difficult" substance, 0·5 g is refluxed with 8 ml of 4:1 methanol–pyridine mixture, cooled, and added to the K.F. vessel, followed by 2 ml of rinsings, all (including the condenser) being guarded by silica gel.

The cost of the reagent and solvent can be appreciable for a long series of tests and some workers use the K.F. titration as a reference method or for special investigations, using other procedures for multiple routine testing. Some object to the smell—it is not desirable to breathe the vapours of methanol and pyridine for long periods. Mitchell[1] examined substances which interfere with the K.F. reaction and suggested means of prevention. Vitamin C interferes, being oxidized to dehydroascorbic acid. The K.F. titration estimates total water, including water of hydration. It is valuable for testing explosives.

Peters and Jungnickel[33] found that methylcellosolve in place of methanol in the K.F. reagent gave greater stability and that direct titration of water in ketones and some aldehydes was possible if a mixture of ethylene glycol and pyridine was used as solvent.

Modified reagents are available for interfering compounds, and a catalyst, *N*-ethylpiperidine, speeds up the estimation and improves the accuracy.[34]

Duncan and Brabson[35] determined free and total water in fertilizers. Free water was obtained by extracting with 1,4-dioxan and titrating the extract with K.F. reagent. Total water was found by azeotropic distillation with n-pentanol and titration of the distillate, the difference being "hydrate water."

Heslop *et al.*[36] described how fertilizers and materials insoluble in methanol may be ground in a closed vessel with a high-speed cutter, followed by direct K.F. titration in the same vessel. Moisture estimation by oven-drying is not suitable when ammonium nitrate is present.

A semi-automatic timed end-point K.F. titrator for liquids and gases is described by Cope, and uses a relay in place of a microammeter.[37] A coulometric microdetermination of water in the range 0·1–2 mg has been described.[38] Archer *et al.*[39] recommended voltage measurement as being more sensitive than current measurement. They also described a totally enclosed titration cell to prevent pick-up of water and avoid end-point drift. A sensitive double electrode system is the subject of a British Patent.[40]

Optical methods—refractometric and infrared

Refractometric methods. The refractive index of a solution can indicate its water content, and refractometers of various types are in regular daily use in industries dealing with syrups, such as the sugar, glucose, jam and confectionary trades. The refractive index of water at 20° is 1·3330 and that of an aqueous solution will be increased according to the amount and nature of the dissolved solids. Tables are available, the most often used being those for sugar, to show the "concentration," *i.e.*, percentage dissolved solids corresponding to a particular refractive index. The water content of clear solutions is given by the difference from 100%. Undissolved material does not affect the refractive index, the refractometer giving only the concentration of the syrup phase. When crystallized sugar or other undissolved material is present the water content found by difference will be too high. For clear syrups the refractometer is extremely useful as it requires only a few drops of sample and a reading is obtained at once with only a minimum of preparation and cleaning. Slightly different values are given by dextrose, fructose, honey and invert sugar. The Corn Refiners' Association Inc.[41] has published corrections for corn syrup, which contains dextrins, according to its dextrose equivalent and mineral matter content.

Tables for sucrose and other sugars are published internationally[42] and various reference books include tables for many other aqueous mixtures.[43]

Readings are usually taken at 20°, which means that hot syrups have to be cooled down to this temperature; alternatively a correction based on temperature can be applied. The Abbe refractometer is a general-purpose instrument incorporating a water-jacket and thermometer to make temperature correction easy. It may have a sugar scale calibrated 0–95%, capable of estimation to 0·1%, but in practice high-boiled solutions approaching the highest concentrations will set hard very rapidly unless kept at a high temperature. Sugar alone at 20° will begin to crystallize at concentrations above 65%. A more practical range for confectionary syrups of mixed sugars is up to 85% concentration, corresponding to a refractive index of approx. 1·503 at 20°.

To correct for the temperature of the refractometer prisms, at 15° 0·4% is added to the per cent of water, and at 25° 0·4% is subtracted. Refractometric tables are based on the mean sodium D lines but instruments have an adjustable white-light compensator so that they can be used under ordinary conditions of illumination. The Abbe instrument can be checked for correct calibration by using pure water at 20° in conjunction with a test-piece of glass of known refractive index. The instrument can have a flow-through cell which is very useful for fast repetition testing of low-concentration solutions in an industrial process.

Simple pocket instruments are available without stand or temperature control, which will give results to about 0·5 % for soft drinks, cordials, wines and malt extracts. Various scales are offered to suit the products to be tested.

The *Projection Refractometer*[44] was designed for on-the-spot testing of products regardless of colour and the presence of solid pip-like material, the sample being merely spread onto the horizontal surface of the glass prism set in a robust rectangular instrument using the principle of internal reflection. The critical angle borderline, observed through a glass window, intercepts the scale reading directly in terms of sugar concentration or "soluble solids." Scales can be read to 0·2 % but dark opaque products (*e.g.*, containing cocoa) cannot be read accurately.

Temperature control, with the instrument in a room at 20° or at constant temperature, is not usually required, because of the weight and bulk of the instrument in relation to the small amount of sample.

Pipeline Refractometers employ the same principles as the projection refractometer but are designed for direct installation in pipelines to give continuous readings. They must withstand considerable pressure and are hydraulically tested to ensure prisms cannot be blown out. Allowance is made for temperature which may be very high in in-line process control.

Immersion Refractometers differ from the Abbe in that the prism is dipped in the test liquid, which is convenient for larger samples. The accuracy is high and the range is correspondingly restricted, but full application may be covered by using interchangeable prisms. A small cylindrical chamber which holds the solution to be tested fits over the prism at the bottom of the instrument. The critical angle borderline due to the difference in refractive index between the prism and the liquid sample is observed on a scale through the eyepiece.

The same instrument can be obtained with a water-jacketed prism box for temperature control, which requires only a few drops of sample. Another option is a small auxiliary prism which can be attached to the main prism to enable liquids of high optical density to be tested, only one drop being required. Another alternative is a flow-cell attachment to provide continual monitoring or rapid measurement of separate samples.

Differential Refractometers are now available with split cells. One half holds a reference solution while the other is used for the test-liquid. The difference in refractive index is measured and this provides greater sensitivity and overcomes the necessity for temperature corrections, if reference and test solutions are at the same temperature.

Infrared absorption. Infrared or near-infrared spectroscopy may be used for water estimation with transmitted or reflected radiation. Making use of reflectance is a fairly recent development and instruments are expensive at present, but there is no physical contact with the test material and continuous monitoring is possible for solids, liquids and gases.

A standard form of instrument will measure up to 30 % water but by use of different filters measurements to almost 100 % are feasible, a flow-through cell being used for liquids.

The principle is that of absorption by water of infrared radiation of specific wavelength, principally 1·93 μm, the extent of absorption on reflectance being compared by photo-cell with a reference beam at a different wavelength (1·7 μm) to compensate to some extent for other factors such as fat. A twin-beam infrared spectrophotometer is used with an attenuator which can control a digital voltmeter to read water content. It is an empirical method, but under best conditions with a fine light-coloured powder, sensitivity can be good (0·05%). The apparatus is in use for paper manufacture. Results are not affected greatly by temperature variations within ±5°, but particle size and chemical composition affect results. Swift[45] and Slight[46] have reported on such an instrument.[47] Keyworth[48] found a wavelength of 1·9 μm most suitable for the measurement of water in methanol, isopropanol, dioxan, glycols and polyols by direct spectrophotometry. He used a differential spectrophotometer with ethylene glycol of known water content to test anti-freeze mixtures. Goulden and Manning[49] determined water in methanol extracts at 1·93 μm and found a coefficient of variation of 0·4% and detectability down to 0·01%. These limitations could be further reduced, if required, by modifications in instrumental technique. Calibration was done by adding known amounts of water to methanol. They proposed the method for dairy products. Uses are very diverse; infrared radiation can be used to measure the water present in steam at high temperature and pressure.[2]

Vapour pressure methods

Indirect and non-destructive methods based on vapour pressure or determination of equilibrium relative humidity (E.R.H.) are in use. Absolute humidity is the mass of water per unit mass of dry air; relative humidity (R.H.) is the ratio of the water vapour pressure in the air to the saturated water vapour pressure, expressed as a percentage. The vapour pressure of the air over a substance in an enclosed space will come into equilibrium with that of the vapour pressure of the substance, as a result of moisture transfer to or from the substance. The change in water content of the substance is negligible, as the mass is usually large in relation to that of the air. In practice the relative humidity of the air in the head space is measured after time has been allowed for equilibrium to be reached. Paper, boards and textiles are often examined in this way. A dial hygrometer can be used over a test-sample in a container and observed through glass. The sample can be large, which is an advantage with paper and similar materials where water distribution is not uniform and very small samples may be unrepresentative. The equilibrium point is easily observed but it may take 30 min to reach for paper and very much longer for other materials. Each type of material will have its own E.R.H./water relationship and this must be determined by a reference method. The E.R.H. method in terms of water content is not very accurate and is useless at the extremes of the range as there is only a small change in vapour pressure for a comparatively large change in moisture. Also it is only the free moisture and not that chemically bound which can be measured. Chipboard with E.R.H. about 65% will have 6–8% water while strawboard at the same E.R.H. will possess 8–12%. A manufacturer or user of paper and board is usually more concerned with E.R.H. and does not necessarily want to know the water content. It is important that paper and board are "normalized" to the ambient humidity around 65% to avoid curling or warping. A sword-type hygroscope—a stainless-steel sheath with hair element and a dial—is available for testing stacks. The "sword" is simply inserted between layers of material and the E.R.H. noted when it reaches a steady value. This will give the water content after suitable calibration and allowance for temperature.

Wet and dry temperature elements (psychrometer) will determine relative humidity and are much used in air-conditioning plants and for testing atmospheres but are not of general application.

Much research has been directed to E.R.H., water activity, and vapour pressure measurements, for food materials for comparison with other methods. The manometric, volumetric, sorption isotherm, sorption rate, and dew-point method have all been tried for special cases, taking advantage of their non-destructive nature, but are slow and require laboratory apparatus and technique. Smith[50] has reviewed the literature. Hickman[51] has also reviewed the subject of humidity measurement.

A 1969 directory lists 62 suppliers of hygrometrical instruments, the types including Assmann, dew-point, diffusion, electrolytic, capacitance, frost-point, hair-type, microwave, and wet and dry.[52] One of the problems associated with relating water to E.R.H. measurements is the hysteresis effect shown by some materials whereby for a given water content the E.R.H. may differ according to whether the sample approaches this water content by taking up or giving off moisture.

Dial hygrometers using hair or parchment elements require frequent calibration. A far more accurate measurement can be obtained by employing an electrical hygrometer.

Electrical Hygrometers were reviewed by Weaver[1] in 1951 and Smith[50] in 1971. The earlier instruments measured the conductivity of a hygroscopic salt solution, lithium chloride. Some time is required for this to attain equilibrium with the head-space to be tested and developments were directed towards reducing the amount of salt solution and obtaining maximum exposure at the sensitive end of the moisture probe. One type uses glass-fibre yarn impregnated with lithium chloride but response is non-linear and limited to a range of 25–90% R.H. The temperature coefficient is large but can be compensated. Aging is also a factor. Anodized aluminium sensors and ferric oxide/chromic oxide films have now been produced for instruments which are more robust, quicker to respond, and possess a smaller temperature coefficient. A thin porous oxide layer on an aluminium rod responds to changes in humidity and can be used with conductance or capacitance instruments. Stability is improved by impregnating the oxide layer with sodium tungstate. Details of the construction, properties, theory, and application of the anodized aluminium hygrometer were given by Jason.[2]

The oxide layer is only a few μm thick and dynamic equilibrium is achieved between the liquid water in the pores and the external water vapour pressure. The sensitivity depends on the thickness of the oxide film and can be very high, but limited to a top range of 90% R.H. Pore size and structure are also important.[53]

The electrical hygrometer will give rapid indication of the R.H. in a gas and hence the water vapour pressure and dew-point when the temperature is known. Published tables will show the amount of water per unit volume.[54] Electrical hygrometers are widely used in air-conditioning installations.

Modern aluminium oxide types are less affected by temperature, dust, and age, but like lithium chloride hygrometers, must be checked in atmospheres of known R.H. This is conveniently done by using the head-space over various saturated salt solutions. Tables are available covering the range 12–98% R.H. over a temperature range of 5–40°.[55] Alternatively, sulphuric acid solutions of known concentration are used.

Where a number of hygrometric moisture meters are in use in an industrial concern it is common practice to check these quickly with a master meter which is laboratory-calibrated.

When testing solids, the measurement of R.H. is delayed by the time required to obtain correct E.R.H. in the head-space over the sample. This may vary from 15 min to more than a day, depending on such factors as weight and size of sample, diffusion rate within the sample, surface area.

The E.R.H. and R.H. can be obtained with a high degree of accuracy, but when related to solids and liquids the accuracy in terms of water percentage is poor for most materials and the range is limited although often suitable for some kind of process or storage control.

Electronic methods

A large and growing number of instruments is now available, designed either for general use or for more specific purposes to meet the demand of industry and commerce for rapid results for process and storage control. Such instruments are called moisture-meters rather than water-meters—the latter meaning flow-recorders. Electrical hygrometers were discussed in the preceding section. Electronics can produce a continuous read-out and sound-alarm or provide servo action if required. The cost varies a great deal—from less than £100 to several thousand pounds, depending on the degree of sophistication, flexibility, and accuracy required. None determines the absolute water content, all have to be calibrated by some reference method for the material to be tested, and zero, scale and other instrument adjustments made. Claims may be made that the accuracy is ±0·1 % when what is meant is that this is the extent of repeatability.

Development of the earlier types based on conductance or capacitance has slowed, but it is still early days for microwave, N.M.R., and radioisotope techniques. Future development lies mainly with the electronics engineer and not the chemist. The latter can state the problem and give help, while industry will indicate the demand on efficiency and economic grounds.

Conductance or capacitance methods. Moisture meters of this class are relatively simple and cheap. They can be mains-operated but many use batteries to make them completely portable, as speed and portability are among their main advantages.

Conductance-type instruments are based on the fact that electrical resistance in the presence of an electrolyte decreases as the water content of non-conducting solids increases. The first electrical instruments were based on this, using Wheatstone bridge circuits for measuring the resistance. A limit is reached when sufficient free water is present to conduct current along a path between the electrodes. The resistance decreases at higher frequencies and an optimum is chosen for the material and range of water content. Temperature correction is necessary. The measurement of resistance or conductance is employed where electrodes have to be clamped or make close contact with materials in bulk such as sheets, planks, timber, *i.e.*, materials in a form difficult to sample on a representative basis, or that at best involve procedures which are very time-consuming. The electrodes are designed for specific purposes and may be needle, hammer or probe types. Roller or profile electrodes are used on conveyor bands, or moving webs of materials.

Calibration may be of an arbitrary scale or in terms of moisture as found by some other method. Repeatability may be only to within ±1 % but the large number of results which can be obtained in a short time, or continuously over a bulk of materials, will average to give a good practical result. Certainly, variations are correctly indicated provided the effective range of the instrument is not exceeded.

A range of special electrodes has been produced for batch or continuous testing of tobacco at various stages of processing; many other commodities may also be tested. Resistance is measured by a milliammeter in a special circuit using a cathode-coupled tube voltmeter with a current amplifier and automatic temperature compensation. It is claimed that this circuit is very stable and that the instruments do not require recalibration even after years of use.

Extracts from soil can be tested for electrical resistance. Soil is shaken with pure isopropanol and the fall in specific resistance of the filtered extract (saturated with dry sodium chloride) measured to give water content. Accuracy to within 1 % absolute is claimed over a wide range, and with a variety of soils. Calibration is carried out by adding water to oven-dried soil.[56] Industrial applications of resistance measurement for continuous moisture determination have been patented recently for wood veneer, paper web, board,[57] and cotton, silk and man-made fibres.[58]

With *capacitance-type* instruments the estimation of moisture in a sample is not so limited as is the case with conductance, and utilizing the electrical property of capacitance widens the scope of the instruments. Capacitance is less affected by variations in salt content and enables a greater range of water contents to be covered for many materials. Water has a very high dielectric constant (81) and when dry matter absorbs moisture its dielectric constant is considerably increased. Plastic ("Perspex") cells between plates act as condensers to which a high frequency current is applied. The cells are removable and may be in various sizes. Two balanced oscillating circuits are used, one fixed at say 18 MHz while the other, which includes the test cell, can be adjusted to balance with the fixed oscillator by use of a variable condenser, the balance being indicated by the brightness of a neon lamp or by a milliameter.

Replacing the air in the cell by the test-sample changes the capacitance, thus requiring adjustment of the variable condenser. Each manufacturer has his own favoured circuits for particular products. General-purpose instruments may have various fixed condensers in the circuits, operated by push-buttons to provide several ranges of readings. The dielectric constant for a given frequency will vary according to the water present only within limits and each manufacturer will recommend suitable ranges up to about 60 %, based on water calibrations, for various types of materials. Outside these ranges the results may be useless, but otherwise repeatability can be good, to within 0·1–0·2 %. The error, as shown by comparing results with standard gravimetric methods, may be 0·5 %, however, for a range of samples even of the same type. Precautions must be taken even to obtain this. Texture, and degree of packing of the material in the cell, are important factors, and so is temperature. It is normal to weigh the sample, although the weight may not be very critical, and use a compression device or plunger for the cell for granular materials or powders such as starch and dried milk. Repeatability and accuracy are reduced in the higher ranges.

Cells commonly hold about 100–400 g. The instruments may record directly in terms of moisture but as the relationship of electrical properties to water-content is different for various types of material, interchangeable plastic moisture scales are used—sometimes multiple ones for convenience on the same instrument. The moisture for a given electrical reading may differ by as much as 3 % for different cereals. Closer agreement can be obtained by coarse-grinding the sample as a preliminary.

Variations in density are more important than temperature. Compensation for specific materials (*e.g.*, flour) can be made by using a radioactive probe designed to measure density, thus circuit correction for particle size and packing makes possible in-line process control, at extra cost.

New apparatus has been designed to measure conductance and capacitance at three separate frequencies simultaneously. One or more of the electrical parameters is related to water, the others compensate for variables such as fat.[59]

Microwave attenuation methods. Development of these methods followed that of the conductance and capacitance instruments and research is still active to improve response specifically for water and to produce satisfactory designs for industry for sample-testing or continuous recording.[60]

The microwave principle is based on the absorption by water of high-frequency radio energy generated by a klystron oscillator. Electromagnetic microwaves of frequency 10^3–10^5 MHz (wavelengths 30 cm–3 mm) can be absorbed and reflected like light. The distance of the receiver from the transmitter is an obvious variable to standardize.

One instrument consists of a transmitter with a frequency of 10,680 MHz operating through waveguides ending in a 3-in. square horn and an attenuator with crystal detector. Microwave absorption is much greater with "free" moisture than with dry substances and so the degree of attenuation can be related on a linear basis to moisture as determined by reference methods, due correction being made for temperature. In actual use for sample-testing, a "Perspex" cell is placed between the transmitter and the receiver, these two parts being fixed on a stand at a predetermined distance. Following the usual adjustments for zero, scale deflection, *etc.*, the degree of attenuation produced by the sample is obtained within seconds in terms of decibels. Slide-rule calculators covering the ranges of temperature (found by thermistor), weight of sample and degree of attenuation, are calibrated for water for the type of material undergoing test. The error is of the order of 0·5% absolute for baked goods (cakes) and Ince and Turner[61] found that texture and density were more important than recipe change. Closer results were obtained for nougat (author's laboratory) by using a 2½-in. deep cell, 5½-in. diameter, taking due note of the weight to compensate for air inclusion. It should be noted that these are rather difficult materials to sample representatively for more orthodox testing, and the microwave apparatus has an important industrial future as more applications are found. The instrument can be calibrated directly in terms of moisture for fixed installations and the product (*e.g.*, milk powder, cereals, and foods in general) can be continuously monitored without contact, damage or loss if passed through "Perspex" pipes between the transmitting and receiving horns.

Temperature and salt content influence microwave attenuation but compensation can be made for both, by using thermistors and conductivity circuits, and research on this is proceeding.[45] Maximum accuracy for water measurement lies within the signal range 7–40 decibels and wavelengths can be selected to bring the attenuations within these limits.

Microwaves have been employed to measure water variations in concrete and brick walls, by using portable battery-operated instruments.[2] Air can be used to fluidize a controlled feed of powder or granular material to maintain a constant density for continuous testing.[62]

NMR methods. Nuclear magnetic resonance is a later development of non-destructive electronic testing (since about 1950). The apparatus produces two magnetic fields simultaneously—a strong field very slowly oscillating about a mean value and a weak constant radiofrequency field perpendicular to the other. Hydrogen nuclei in the liquid phase of a sample absorb energy from the radiofrequency field and at a certain value of the strong field strength the rate of absorption is at a maximum in relation to the particular frequency and the nuclei are said to be in a state of resonance. Nuclei in solids are immobile and cannot resonate. The field strength and frequency of the apparatus can be arranged so that only hydrogen nuclei resonate.

Hydrogen nuclei in foods and similar materials are primarily in the oil, fat, or water present but those in carbohydrates and protein will respond if these substances are in the liquid phase. High-resolution instruments are required to distinguish between hydrogen in fat and water. NMR is proving very useful for the direct monitoring of fat in food manufacturing processes (*e.g.*, chocolate) but in the case of water alternative cheaper methods are available. Research continues and there may be worthwhile applications for high-moisture materials where other electronic methods are not suitable, also where the oil content is low, or known and constant. The NMR signal is calibrated against results obtained by reference methods. The use of NMR apparatus is quick and simple but the equipment and theory are complex.[2]

A portable high-resolution broad-line NMR spectrometer has recently been introduced.[63] The test-material is weighed into a sample tube and the NMR signal calculated per gram for reference to moisture tables. NMR apparatus has been used with static and moving beds of coal and coke for water measurement with an error of about 1%.[64] NMR may be used to distinguish between free and bound water, if the temperature is reduced to below freezing point.

Electrolytes may affect NMR readings and when soils are tested the leaching out of electrolytes over a period can introduce errors.

Nuclear radiation methods. Fast neutrons emitted from a radioactive source in a probe are slowed down by elastic collisions with the hydrogen nuclei of water in a moist material, which results in the formation of a cloud of slow neutrons, the density of which (as measured in counts/sec) can be related to the water content. This is known as neutron moderation or scattering. The atomic nuclei of matter in general will cause scattering but to a much lesser extent. Water indication is by proportion by volume of the moist substance and to determine proportion by weight it is necessary to correct for density, usually with a gamma-radiation source and detector. A dual neutron–gamma instrument will combine the output signals from both detectors to give water percentage by weight. The inclusion of such a compensating probe can reduce errors to about 1%.

Although nuclear-radiation gauging can be used for testing many materials the greatest application has been in the examination of soil. It offers greater precision than standard gravimetric methods because of the large test sample (a cubic yard—about 1 ton) which can be tested *in situ* without disturbance.

The effect of soil composition is significant, as the detector is for hydrogen nuclei and is not specific for water; nevertheless, for known areas the instrument can be valuable and it is simple to make tests at varying depths.

The difficulties of calibration (laboratory, field, and by simulation) for soil were discussed at the U.S.A. 1963 Symposium.[2] When composition and density remain constant, either a neutron or gamma gauge can be used for monitoring water content. Soane[65] reported results of tests using dual (high and low) energy gamma-ray transmissions for simultaneous measurement of water content and dry bulk-density of soil.

The Institute of Hydrology has developed with the Atomic Weapons Research Establishment, Aldermaston, an instrument using the neutron-scattering technique for soil-moisture measurement. Besides the probe there are a shielded transport carrier and a ratemeter. The standard aluminium alloy access tube immersed in water shows about 850 counts/sec, while in air it is about 5 counts/sec. The effect of temperature variation between −10 and +40° is claimed to be insignificant (less than 2 counts/sec).

The probe carries 50 mCi of americium/beryllium and a slow-neutron detector, E.H.T. generator and pulse-shaping circuits, powered by a battery so that the instrument is easily portable.[66] The use of radiation gauging for water monitoring is being extended where there are special industrial problems with such materials as coal, coke, iron ore, sinter mix, concrete.

Instruments have also been designed for food testing.[67]

Miscellaneous methods

The foregoing shows the main groups of methods and techniques employed for water measurement but for every type of material for which a knowledge of the water content is required there will be found a specific method devised with a view to obtaining a quick result under non-laboratory conditions. All are empirical and rely on reference methods carried out under closely controlled laboratory conditions. Unfortunately, this is not always understood by semi-skilled workers using the instruments, who tend to have implicit faith in the dial readings and neglect the apparatus or delay too long the recalibration made necessary by wear and the deterioration produced by time.

Much literature has been published on various methods of testing soil, sand, gravel, coal, and similar materials because of their commercial importance and the problem of reducing such bulky and variable materials to the small representative samples which are normally required by the conventional reference methods. Loss of weight after heating in a non-volatile oil and after evaporating the water with burning alcohol have been used. Water present will influence to some extent a material's physical, chemical, or electrical properties and each type of substance will have one or more parameters suitable for relating to water to give a result satisfactory for commerce.

Density or specific gravity methods are much used for solutions of simple substances such as sucrose, salt, and soluble chemicals in general, and tables relating to aqueous mixtures are published together with temperature corrections. As an alternative to hydrometers or pycnometers a "moisture balance" will accurately determine density or specific gravity by the buoyancy principle, using a plummet suspended in the test-solution. If the test-substance is in the solid state, it may be weighed in a liquid of known specific gravity (Archimedes' principle). Success with the latter method presupposes no pores or voids in the solid substance, and insolubility in the liquid.

For general testing of insoluble composite material the water can often be extracted with ethanol or methanol and a result calculated from a change in density or boiling point, or the extract may be used for a Karl Fischer titration. Acetone, isopropanol, dioxan, dimethylformamide and glycerol are other extractants which have been used and the possibilities are numerous as the extracts can be tested by many of the methods previously mentioned and the result calculated back to give the water-content of the original solid.

Gases can be simply tested in the laboratory by passage through weighed U-tubes containing phosphorus pentoxide, calcium sulphate or calcium oxide desiccant, alternatively by the Karl Fischer method, or by G.L.C. using a thermal conductivity detector. Dew-point can also be determined accurately and is used to standardize other techniques, but industrially, wet and dry bulb hygrometers or hair-type hygrometers are used for immediate measurement and continuous recording. Electrical hygrometers have become very important because of their versatility.

Miscellaneous methods include application of rise in temperature due to chemical reaction with sulphuric acid, thermal conductivity, specific heat, surface tension or suction and the use of absorbent blocks. The last two are made use of for measurements of water in soil. The reading produced by a buried porous pot filled with water and connected to a vacuum gauge will indicate water-content, although influenced by soil particle-size and degree of packing.[68] Saturated soil will show a reading of 30–60 mmHg; drought conditions are indicated by over 300 mmHg. Watson[69] has described a modern field tensiometer.

Absorbent blocks can be buried in soil and the weight at equilibrium made to give the water content, but more conveniently the blocks may be tested *in situ* for electrical resistance.

One well-known method based on chemical reaction is that using calcium carbide. It is popular for "field testing" because of its cheapness, speed and convenience. The sample is weighed and shaken with calcium carbide in a sealed pressure vessel fitted with a dial pressure gauge, the maximum pressure produced by the acetylene generated being related to water by suitable calibration.[70] There are variations using this chemical method, *e.g.*, the volume of the gas may be measured, or the loss in weight determined.

Various workers have sought an alternative to the K.F. titration. When dissolved in ethylenediamine, water acts as an acid and can be titrated under a nitrogen atmosphere.[71]

The use of G.L.C. is proposed for low amounts of water in gases and liquids. Columns with 80–100 mesh Porapak at 140° with hydrogen as carrier-gas are claimed to give optimum results, but sensitivity can change and fresh calibration is required.[72]

Water in air and natural gas can be estimated down to 50 ppm by using polytetrafluoroethylene column packed with Porapak Q and employing a thermal conductivity detector.[73]

The cloud-point or critical solution temperature of a two-component system such as dry methanol in n-hexane is dependent on traces of water, and thus common solvents such as methanol, ethanol, acetone, ethyl methyl ketone and dioxan may be tested for water content by using this technique with controls. Test samples may be 10–50 μl in volume but the number, amounts and identity of the components must be known for calibration to be applicable.[74]

Pande[75] has described a new micro-determination based on hygrophotography.

REFERENCE METHODS

Standardized reference methods are published by various official bodies (see list below) only for specified materials—there can be no one all-embracing method, as this review will have made clear. Where there is no official reference method for a product of commercial importance, firms or their Research Associations will often have agreed upon one. The most favoured, as being of widest application, is a drying method with or without vacuum, subject to limitations as described in the appropriate section above. At one time there was reluctance to include vacuum procedures with reference methods, as this meant stipulating some particular manufacturer's vacuum oven, with obvious objections, but this has now been overcome by setting out the precise conditions required. Drying has the advantage that in most cases it can be investigated so that conditions can be set to yield a result close to the "true" water content, and the apparatus is simple and cheap, apart from the balance, which is part of the general laboratory equipment anyway. Also any range of water can be measured and almost any amount of sample taken.

The Karl Fischer method comes closest to measuring absolute water content, and will cover any range, although accuracy is reduced at high levels because aliquots have to be taken to keep the amount of water within the best range for titration. There is not wide adoption of the Karl Fischer test as an official one, but there is a present-day trend toward this, or it is given as an alternative method. Earlier policy with official tests has always been to keep them simple for the widest possible use by all concerned. The K.F. test serves a very useful purpose in deciding the conditions necessary for the more simple drying methods.

Distillation by the Dean and Stark method has been taken as an official method for some materials and it has obvious claims in this respect.

Refractometric methods are taken as "standard" in some trades but their use is obviously restricted.

Various physical properties, when accurately measured under laboratory conditions, can estimate absolute water but under conditions so restricted that these methods are never adopted as official although of course, like the K.F. test, they can serve an important function in checking the accuracy of other accepted methods.

None of the electrical methods can be used as official tests as they are dependent on calibration by other procedures.

The following publish official methods in either the U.K. or U.S.A.

British Standards Institution, Park Street, London, W.1.
British Pharmacopoeia, General Medical Council, Pharmaceutical Press, London.
The Society for Analytical Chemistry, Savile Row, London, W.1.[76]
Association of Official Analytical Chemists, Washington, D.C.[77]
Pharmacopoeia of the U.S.A., Mack Publishing Co., Easton Pa.
National Formulary, American Pharmaceutical Association, Washington.
National Bureau of Standards, U.S.A. Government Printing Office.
American Society for Testing and Materials (A.S.T.M. Standards), Philadelphia.

In addition there is a large number of Trade Research Associations which publish recommended methods for water or moisture measurement. Some of these methods are more or less identical but not all. Usually the official tests are the result of collaboration by interested parties and, although without legal authority, they provide a common ground between vendor and purchaser where water content is stipulated and it would be clear in arbitration what is meant and intended when, for example, a British Standard is quoted. The various Trade Research Associations give details of recommended methods and also from time to time investigate and critically examine the performance of various instruments. Their publications are sometimes only available to member companies but Research Reports can be purchased.

Apart from the U.K. and the United States there are, of course, many other countries interested in standardization. International organizations in Brussels, Geneva, and Zurich become increasingly important.

Close international standardization will not be easy. A B.S.[78] for coal and coke gives nine procedures for water estimation, if all variations of sample weight, temperature and time are included, depending on type of coal and mesh size. Two use Dean and Stark apparatus, one uses a drying process with nitrogen, another uses vacuum, the others use simple drying to constant weight.

The International Standards Office, with regard to starch, states moisture content equals loss in mass undergone by the material under the specified conditions of the test but a B.S.[79] prefers the term "loss in mass on drying" in place of "moisture content" in this statement. Three methods are given, drying at 130° for $1\frac{1}{2}$ hours and finally to constant weight (further loss <5 mg), drying at 100° for 4 hr and finally to constant weight, and drying at 73° at 10–20 mmHg for 24 hr to constant weight (further loss <1 mg).

To review all reference methods in all major countries and to bring them on to an internationally agreed basis will be a great task but will become increasingly important as more and more materials become subject to standard methods of testing. Deviations should be as few as possible and agreement should not be hindered by trade practices and traditions.

International symposia will continue to review methods and techniques. In the U.K. there is the annual Physics Exhibition organized by the Institute of Physics and the Physical Society, also the parallel exhibition of the Scientific Instrument Manufacturers' Association.

As regards the future there is little likelihood of any great change in drying methods, and these and the Karl Fischer and distillation techniques are the basic reference methods. No new fundamental principle has been widely established for water measurement since NMR and nuclear radiation techniques were introduced over 20 years ago, except that of infrared absorption by reflectance.

APPENDIX

The determination of water in rocks and minerals is rather different from the determination of moisture in general, in that the water present may be either loosely or firmly held, and different methods are required for determination of the two kinds. The loosely held or interstitial water is usually defined as the amount of water evolved on heating the sample at some defined temperature such as 105° or 110°. For this purpose the oven-drying methods may be used, or the Dean and Stark method. The drying methods are not suitable, however, if other volatile substances are also present in the rock, or if the rock contains large proportions of easily oxidized species such as ferrous iron, but such difficulties may be overcome by absorbing the evolved water, in a closed system such as that described by Jeffery and Wilson.[80] Similar apparatus, modified to allow for heating the sample to the higher temperatures necessary, may be used for determining the total water, *i.e.*, the interstitial and the "constitutional water".[80–82] In determining the total water it is necessary to avoid errors due to evolution of carbon dioxide, hydrogen fluoride, sulphur compounds *etc.*, and for this purpose various additives or absorbents can be used to retain or collect these species. The simplest method for total water determination is the Penfield method[83] or one of its modifications,[84–87] used with or without a flux such as litharge or sodium tungstate. In this method the sample is heated to high temperature in a hard glass tube and the water evolved is condensed or absorbed, and then weighed either by difference or directly. Care must be taken in preparation of the sample when water is to be determined in rocks: if the grinding is too fierce, water may be lost, but on the other hand the great increase in surface area on comminution of the sample may increase the amount of hygroscopic moisture taken up.[88] With the closed systems, a blank correction must be made for residual water in the gas used as carrier-gas for the water vapour evolved, and the sample size must be large enough for variations in the blank to be insignificant as a source of error.

Acknowledgement—Grateful acknowledgement is made to colleagues of J. S. Fry & Sons and Cadbury Bros. Ltd., for assistance with this Review and to the University of Bristol for facilities provided.

Zusammenfassung—Die komplizierte Natur des Themas und die bei der Bestimmung von Wasser in den vielen zu prüfenden Materialien auftretenden Probleme werden erklärt. Die verschiedenen vorhandenen Methoden werden klassifiziert, Übersichten über die Arbeitstechniken gegeben und ihre Anwendungsmöglichkeiten und -grenzen gezeigt. In vielen Materialien ist die Bestimmung der absoluten Feuchte nicht möglich und es muß ein Kompromiß geschlossen werden. Gewerbe und Industrie brauchen für viele Prozesse und Produkte rasche Ergebnisse; daher werden in immer größerem Ausmaß optische oder elektronische Verfahren in Verbindung mit Vergleichsmethoden verwendet. Für amtliche Zwecke muß Einigkeit über die Bestimmungsmethode erzielt und diese im einzelnen festgelegt werden. Weitergehende Fortschritte bei der internationalen Standardisierung sind sehr wünschenswert.

Résumé—La complexité du sujet, et les problèmes impliqués dans le dosage de l'eau dans les nombreux produits qui doivent être essayés sont expliqués. Les diverses méthodes disponibles sont classées, leurs techniques résumées, et leurs applications et limitations indiquées. Dans de nombreux produits, le dosage de l'humidité absolue est impossible et un compromis doit être accepté. Le commerce et l'industrie requièrent des résultats rapides pour de nombreux procédés et produits, et des méthodes optiques ou électroniques sont utilisées de manière croissante conjointement aux méthodes de référence. Pour les usages officiels la méthode de dosage doit être agréée et exposée en détail. Il est trés désirable que davantage de progrés soit fait dans la standardisation internationale.

REFERENCES

1. 1951 Symposium, American Chemical Society, Chicago. C. O. Willits, *Anal. Chem.*, 1951, **23**, 1058. W. R. Fetzer, *ibid.*, 1951, **23**, 1062. J. Mitchell, *ibid.*, 1951, **23**, 1069. E. R. Weaver, *ibid.*, 1951, **23**, 1076.
2. A. Wexler, Editor-in-Chief, *Humidity and Moisture, Measurement and Control in Science and Industry*, 4 Vols., Reinhold, New York; Chapman & Hall, London, 1965.
3. P. J. Geary, *Measurement of Moisture in Solids*, SIRA Institute, Chislehurst, Kent, 1970.
4. J. W. White, *J. Assoc. Offic. Anal. Chemists*, 1969, **52**, 729.
5. Glen Creston, Stanmore, Middlesex, U.K.
6. S. Cotson and D. B. Smith, Editors, *Freeze-drying of Foodstuffs*, Columbine Press, London, 1963. R. J. C. Harris, Editor, *Freezing and Drying*, Institute of Biology, London, Report of 1951 Symposium. R. J. C. Harris, Editor, *Biological Applications of Freezing and Drying*, Academic Press, New York, 1954. A. L. Tappel, *Anal. Chem.*, 1954, **26**, 1671.
7. *Liquid Milk*, British Standard, 1963, No. 1741.
8. *Performance Requirements for Electrically Heated Laboratory Drying Ovens*, British Standard, 1955, No. 2648.
9. *Condensed Milk*, British Standard, 1951, No. 1742.
10. *Dried Milk*, British Standard, 1951, No. 1743.
11. *Gelatines*, British Standard, 1959, No. 757 (Draft Revision 1971).
12. C. F. M. Fryd and P. R. Kiff, *Analyst*, 1951, **76**, 25.
13. Air Flow Ovens, Barlow & Whitney, Bleckley, London.
14. Drying Oven and Balance, Voss Instruments Ltd., Maldon, Essex, U.K.
15. K. Bauer, *Pharm. Acta. Helv.* 1968, **43**, 273; *Anal. Abstr.* 1969, **17**, 1659.

16. Mytron Moisture Tester (German), F. Copley & Co., Nottingham, U.K.
17. Townson & Mercer Ltd., Croydon, U.K.
18. Stanton Instruments Ltd., Oxford Street, London, W.1.
19. P. L. Waters, *Nature*, 1956, **178**, 324.
20. Gallenkamp & Co. Ltd., London.
21. Edwards High Vacuum Ltd., Crawley, Sussex, U.K.
22. British Patent No. 830525, Townson & Mercer Ltd., Croydon, 1960.
23. E. W. Dean and D. D. Stark, *Ind. Eng. Chem.*, 1920, **12**, 486.
24. T. Barr and J. I. Yarwood, *Chem. Ind. London*, 1957, **76**, 803.
25. *Dean & Stark Apparatus*, British Standard, 1952, No. 756.
26. M. K. Meredith, S. Baldwin, and A. A. Andreasen, *J. Assoc. Offic. Anal. Chemists*, 1970, **53**, 812.
27. S. Harel and A. Talmi, *Anal. Chem.*, 1957, **29**, 1694.
28. P. A. Alsop and M. J. Wadsworth, *Analyst*, 1969, **94**, 330.
29. K. Fischer, *Angew. Chem.*, 1935, **48**, 394.
30. D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., *J. Am. Chem. Soc.*, 1939, **61**, 2407.
31. "Analmatic" Karl Fischer Titrator, Baird and Tatlock Ltd., London, W.1.
32. *Karl Fischer Method*, British Standard, 1970, No. 2511.
33. E. D. Peters and L. J. Jungnickel, *Anal. Chem.*, 1955, **27**, 450.
34. *Moisture Determination by the Karl Fischer Reagent*, 2nd. Ed. British Drug Houses Ltd., Poole, 1969.
35. R. D. Duncan and J. A. Brabson, *J. Assoc. Offic. Anal. Chemists*, 1969, **52**, 1127.
36. A. M. Heslop, J. M. Skinner and A. C. Docherty, *Analyst*, 1969, **94**, 681.
37. B. Cope, *Analyst*, 1968, **93**, 436.
38. R. Karlsson and K. J. Karrman, *Talanta*, 1971, **18**, 459.
39. E. E. Archer, H. W. Jeater and J. Martin, *Analyst*, 1967, **92**, 524.
40. British Patent, No. 1138113, A.E.I., 1967.
41. Corn Refiners' Association Inc., Connecticut Avenue, N.W. Washington.
42. C. A. Browne and F. W. Zerban, *Physical and Chemical Methods of Sugar Analysis*, 3rd Ed., Chapman & Hall, London, 1941. *Refractometric and Density Scales of Sugar Solutions*, International Commission for Uniform Methods of Sugar Analysis (I.C.U.M.S.A.), Brussels.
43. *Handbook of Chemistry & Physics*, Chemical Rubber Co., Ohio, U.S.A., 1970.
44. Bellingham and Stanley Ltd., Markfield Road, London, N.15.
45. J. R. Swift, *Progr. Appl. Chem.* 1969, 318.
46. H. Slight, *Proc. Inst. Food Sci. Tech.*, 1969, 142.
47. Pier Optical Moisture Tester, Shandon Control Systems Ltd., Willesden, London, N.W.6.
48. D. A. Keyworth, *Talanta*, 1961, **8**, 461.
49. J. D. S. Goulden and D. J. Manning, *Analyst*, 1970, **95**, 308.
50. P. R. Smith, *B.F.M.I.R.A. Scientific & Tech. Survey*, No. 70, 1971.
51. M. J. Hickman, *Notes on Applied Science*, No. 4, 1970 (N.P.L.) H.M.S.O., London.
52. Purchasing Directory, Instruments, Electronics, Automation, 1969, Morgan-Grampian, West Wickham, Kent, U.K.
53. British Patent, No. 947857, J. L. Saw Ltd., 1964.
54. J. Glaisher, *Hygrometrical Tables*, Taylor & Francis, London. *Hygrometrical Tables for Relative Humidity, Vapour Pressure, and Dew Point*, Meteorological Office, H.M.S.O., London. *Hygrometrical Data for Air*, Institution of Heating and Ventilating Engineers, London. C. F. Marvin, *Psychrometric Tables for Obtaining Vapour Pressure, Relative Humidity and Temperature of Dew Point*, U.S. Dept. of Commerce, Weather Bureau.
55. L. B. Rockland, *Anal. Chem.*, 1960, **32**, 1375.
56. V. K. Leley, N. J. Sawarkar and L. K. Badwal, *Analyst*, 1971, **96**, 460.
57. British Patent, No. 1138592, 1969.
58. British Patent, No. 1138224, 1968.
59. British Patent, No. 1132763 Rowntree & Co. Ltd., York, 1968.
60. Microwave Instruments Ltd., Shiremoor, Northumberland, U.K. Associated Electrical Industries (G.E.C.) New Parks, Leicester, U.K
61. A. D. Ince and A. Turner, *Analyst*, 1965, **90**, 692.
62. British Patent, No. 1122987, 1964, 1968.
63. Newport Instruments Ltd., Newport Pagnell, Bucks., U.K.
64. W. R. Ladner and A. E. Stacey, *Brit. J. Appl. Phys.*, 1962, **13**, 136. W. R. Ladner, *Instr. Practice*, 1964, **18**, 1039.
65. B. D. Soane, *Nature*, 1967, **214**, 1273.
66. Wallingford Soil Moisture Probe, Pitman Ltd., Weybridge, Surrey, U.K.
67. Moisture Meter, Nuclear Enterprises Ltd., Sighthill, Edinburgh, U.K. EAL Moisture Meter, Electronic Associates Ltd., Burgess Hill, Sussex, U.K.

68. W. S. Rogers, *J. Agric. Sci.*, 1935, **25**, 326.
69. K. K. Watson, *J. Hydrology*, 1967, **5**, 33.
70. B. D. Soane and C. Calissendorff, *Rhodesia Agric. J.*, 1960, **57**, 386. "Speedy" Moisture Tester, T. Ashworth & Co. Ltd., Townson & Mercer Ltd., U.K.
71. W. R. Heumann, A. Bouchard and F. D. Rochon, *Anal. Chem.*, 1968, **40**, 1529.
72. G. M. Neumann, *Z. Anal. Chem.*, 1969, **244**, 302.
73. H. S. Myers, *Gas. Los. Ang.*, 1968, **44**, (5) 60; *Anal. Abstr.*, 1969, **17**, 2225.
74. D. W. Rogers and J. Scher, *Talanta*, 1969, **16**, 1579.
75. A. Pande, *Lab. Pract.*, 1971, **20**, 117.
76. *Official, Standardised, and Recommended Methods of Analysis*, 1963, Soc. Anal. Chem., Heffer, Cambridge, 1963.
77. *Official Methods of Analysis*, 1970, Assoc. Offic. Anal. Chemists.
78. *Coal and Coke*, British Standard, Parts 1 & 2, 1957, No. 1016 Parts 3 and 4 added 1965.
79. *Starch*, British Standard, 1970, No. 4628.
80. P. G. Jeffery and A. D. Wilson, *Analyst*, 1960, **85**, 749.
81. A. W. Groves, *Silicate Analysis*, 2nd Ed., p. 95. Allen and Unwin, London, 1951.
82. J. P. Riley, *Analyst*, 1958, **83**, 42.
83. S. L. Penfield, *Am. J. Sci.*, 1894, **48**, 31.
84. S. Courville, *Can. Mineralogist*, 1962, **7**, 326.
85. C. O. Harvey, *Bull. Geol. Surv. Gt. Brit.*, 1939, No. 1, 8.
86. L. Shapiro and W. W. Brannock, *Anal. Chem.*, 1955, **27**, 560.
87. A. D. Wilson, *Analyst*, 1962, **87**, 598.
88. W. F. Hillebrand, *U.S. Geol. Surv. Bull.*, No. 700, 1919.

Talanta, 1972, Vol. 19, pp. 1549 to 1554. Pergamon Press. Printed in Northern Ireland

NUCLEAR MAGNETIC RESONANCE ANALYSIS OF PHARMACEUTICALS*—VII

DETERMINATION OF AMINOPHYLLINE IN TABLETS

JOHN W. TURCZAN, BRUCE A. GOLDWITZ and JAMES J. NELSON
Food and Drug Administration, U.S. Department of Health, Education and Welfare, 850 Third Avenue, Brooklyn, New York 11232, U.S.A.

(*Received* 17 *March* 1972. *Accepted* 28 *April* 1972)

Summary—An NMR procedure is described by which theophylline and ethylenediamine are simultaneously determined in aminophylline tablets. t-Butyl alcohol was chosen as the internal standard and 4% ammonia–0.3% potassium cyanide in deuterium oxide was the solvent. The solvent system was selected to deal with the problems of solubility of the theophylline, overlapping of the components' resonance signals, and potential interference from metal impurities. Known standard and commercial preparations were determined and the results compared with those obtained by alternative procedures. The technique, when applied to the determination of aminophylline in tablets, is rapid, simple and specific and has an error of 1–2%.

THE DETERMINATION of aminophylline, a mixture of theophylline and ethylenediamine in the ratio 2:1, has been widely discussed. The theophylline content is usually determined and expressed as aminophylline. The analysis of this drug involves a variety of analytical techniques. Aminophylline has been assayed gravimetrically[1] by extraction of theophylline with a chloroform–isopropyl alcohol mixture, and subsequent weighing of the residue. Other methods include both colorimetry[2] and ultraviolet spectrophotometry.[3–8] A potentiometric titration approach to the determination of theophylline alone, and in combination with other drugs, has been investigated by Bartilucci and Discher[9] and others.[10–12] Sarsunova and Tölgyessy[13] have determined aminophylline and theophylline by means of a radiometric titration of the purines, using $^{110}AgNO_3$ to form the insoluble silver salts. The activity of the ^{110}Ag in the solution is then plotted *vs.* the volume of titrant used.

Theophylline has been determined electrochemically by Dušinský and Čavaňák,[14] Yashino[15] and Kalinowska.[16] Methods of complexation of theophylline with copper with subsequent gravimetric or titrimetric determination of the complex have been studied by Runti,[17] Plumel[18] and Blagojević.[19] A non-aqueous titration procedure for the analysis of aminophylline, developed by Medwick and Schiesswohl,[20] involves the differential titration of theophylline and ethylenediamine as a mixture of bases. Non-aqueous titration methods for aminophylline[21–23] and theophylline[20] in combination with other drugs have also been examined.

Other techniques used in the determination of aminophylline and theophylline are aqueous titration as a weak acid in the presence of Thymol Blue[25] and an aqueous

---

* *Other titles in this series are:*

I.—J. W. Turczan and T. C. Kram, *J. Pharm. Sci.*, 56(12), 1643–1645 (1967).
II.—T. C. Kram and J. W. Turczan, *J. Pharm. Sci.*, 57(4), 651–652 (1968).
III.—T. C. Kram and J. W. Turczan, *FDA By-Lines*, 2(3), 105–130 (1971).
IV.—J. W. Turczan and T. Medwick, *J. Pharm. Sci.*, 61(3), 434–443 (1972).
V.—J. W. Turczan and B. A. Goldwitz, *J. Pharm. Sci.*, 61(4), 613–615 (1972).
VI.—J. W. Turczan and B. A. Goldwitz, *J. Pharm. Sci.*, 61(8), August (1972).

thermometric titration of aminophylline with silver nitrate.[26] An NMR method for the determination of theophylline in the presence of other xanthines was reported by Rehse.[27]

The official method (USP XVIII[28]) for aminophylline in tablet form involves the precipitation of theophylline as a silver complex and subsequent back-titration of the excess of silver nitrate with ammonium thiocyanate. In a separate USP procedure, ethylenediamine is determined by titrating an amount of aminophylline with hydrochloric acid to a Methyl Orange end-point. It has been reported [29,30] that the USP assay has a source of error attributable to the solubility of the silver theophylline complex in the ammonia solution used. The cooling step in the official procedure thus becomes a critical factor during the filtration and washing of the complex before the titration.

An alternative procedure presented here uses NMR spectroscopy. By addition of an internal standard and solvent extraction, we have quantitatively analysed many high-dosage pharmaceuticals. The NMR spectrum identifies the active ingredients, contributing to the specificity of the method.

The components of aminophylline in tablet form were assayed by this technique. Many of the results were compared with those obtained by the official procedure and by an ultraviolet spectrophotometric method for theophylline. The NMR procedure is simple, specific, accurate and precise.

EXPERIMENTAL

Apparatus

A Varian A-60 NMR spectrometer equipped with a V-6031 variable-temperature probe having a six-turn insert was used. All spectra were scanned at a probe temperature of 42°.

Reagents

Standard. Aminophylline working standard (USP assay values: moisture 4·06%, theophylline 86·3% on anhydrous basis, ethylenediamine 14·4% on anhydrous basis).

Internal standard. t-Butyl alcohol, 99%.

Solvent. Deuterium oxide, 99·8% isotopic purity, Mallinckrodt Chemical Works, St. Louis, Missouri.

Ammonia solution, sp. gr. 0·880.

Potassium cyanide

Samples. Aminophylline tablets, 1·5 and 3 grains, from various commercial sources.

Procedure

Weigh and finely powder not less than 20 tablets. Weigh accurately a portion of the powder equivalent to about 200 mg of aminophylline into a glass-stoppered centrifuge tube. Add about 9 mg of reagent-grade potassium cyanide and about 50 mg (accurately weighed) of the t-butyl alcohol internal standard. Fill the tube to approximately the 3-ml mark with deuterium oxide. Add about 10 drops of ammonia solution, stopper the tube and shake for 2 min. The tube may be warmed to aid dissolution. Centrifuge to separate the solution from the excipients. Transfer about 0·4 ml of the solution to an analytical NMR tube. Place in an NMR spectrometer and obtain the spectrum, adjusting the spin-rate so that no spinning side-bands occur between 1·1 and 1·5 ppm and between 2·6 and 3·8 ppm on the delta scale. All peak field positions are referred to sodium 2,2-dimethyl-2-silapentane sulphonate (DSS) as 0 ppm. Integrate each of the peaks of interest at least five times.

The amounts of theophylline and ethylenediamine may then be calculated individually as follows:

$$\frac{\text{mg theophylline}}{\text{tablet}} = \frac{A_{\text{th}}}{A_{\text{tba}}} \times \frac{\text{E.W.}_{\text{th}}}{\text{E.W.}_{\text{tba}}} \times \frac{\text{mg t-butyl alcohol}}{\text{mg sample}} \times \text{A.T.W.}$$

$$\frac{\text{mg ethylenediamine}}{\text{tablet}} = \frac{A_{\text{ed}}}{A_{\text{tba}}} \times \frac{\text{E.W.}_{\text{ed}}}{\text{E.W.}_{\text{tba}}} \times \frac{\text{mg t-butyl alcohol}}{\text{mg sample}} \times \text{A.T.W.}$$

where A_{th} = integral value of the signal representing theophylline
A_{ed} = integral value of the signal representing ethylenediamine
A_{tba} = integral value of the signal representing t-butyl alcohol
E.W.$_{th}$ = formula weight of theophylline/6 = 30·03
E.W.$_{ed}$ = formula weight of ethylenediamine/4 = 15·02
E.W.$_{tba}$ = formula weight of t-butyl alcohol/9 = 8·236
A.T.W. = average tablet weight

The amount of aminophylline can be calculated from the theophylline content by multiplying the weight of theophylline (mg) by 1·267, representing the formula weight of aminophylline containing two molecules of water of hydration and divided by twice the formula weight of theophylline.

RESULTS AND DISCUSSION

The choice of a solvent is more complex than in the usual NMR procedure. The solubility of theophylline in deuterium oxide is fairly good, but some theophylline precipitates from solution as soon as carbon dioxide from the atmosphere is absorbed. Furthermore, the absorption peak due to ethylenediamine partially overlaps one of the two sharp singlet peaks due to the two methyl groups on theophylline (Fig. 1*a*). In order to maintain the solution at an alkaline pH to prevent the precipitation of theophylline and to separate the spectrum resonance signals due to theophylline and ethylenediamine, deuterium oxide containing 4% ammonia was used as a solvent. This solvent proved satisfactory for analysis of aminophylline powder, but not for the tablet samples (Fig. 1*b*) where the ethylenediamine peak was too broad for integration. This behaviour was attributed to complex formation between ethylenediamine and a heavy metal impurity present in the tablets. The presence of iron was shown by the formation of a pink colour with thiocyanate. The same broadening was noted when iron(III) was added to ethylenediamine in the same solvent. Competitive complexation was used in order to prevent the undesirable complexation. Cyanide (as the potassium salt) was added to complex iron(III) (or other heavy metals) thereby displacing ethylenediamine and sharpening the absorption line (Fig. 1*c*). The solvent used was 4% ammonia in deuterium oxide containing about 3 mg of potassium cyanide per ml.

A single internal standard, t-butyl alcohol, was satisfactory for all analyses. This alcohol was easily soluble in the solvent and provided a strong signal at a convenient upfield position, thereby resulting in unambiguous identification and interference-free quantitative analysis.

Figure 1*c* shows a spectrum of aminophylline obtained under the recommended analytical conditions. The amounts of each component are calculated from the integration of the singlets (at approximately 3·30 and 3·45 ppm) due to the two methyl groups of theophylline bonded to the nitrogen ring at positions 3 and 1 respectively, the singlet at approximately 2·90 ppm attributed to the four methylene protons of ethylenediamine, and the singlet at approximately 1·30 ppm due to the nine methyl protons of t-butyl alcohol. The other absorption bands at about 4·7 ppm and about 7·50 ppm are ascribable to the HDO in the solvent mixture and the theophylline proton at position 8 on the ring.

A group of known aminophylline mixtures was analysed and the results are summarized in Table I. The NMR results were compared with those obtained by the USP method as well as by a non-aqueous titration procedure.[20] The procedure is both

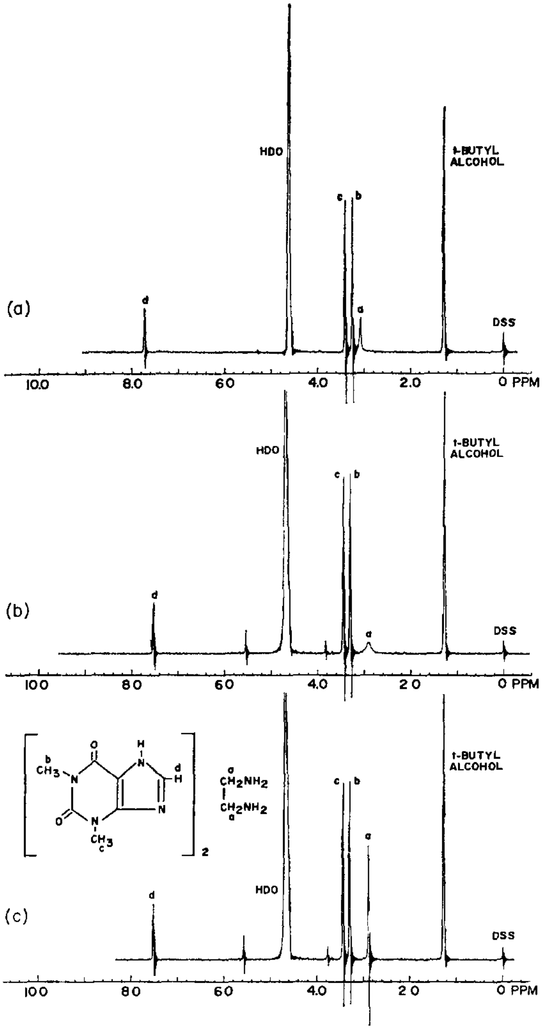


Fig. 1

accurate and precise with relative standard deviation of 0·5% for the theophylline and 0·2% for the ethylenediamine. The relative proportion of aminophylline to t-butyl alcohol has no significant bearing on the accuracy of the determination for the range shown in Table I. The lower results obtained by the USP assay can be attributed to the slight solubility of the silver–theophylline precipitate in ammonia solution. When compared with the USP procedure, the NMR method is simpler, faster, and more specific. An analysis of the two components can be performed in one operation, thus avoiding the two titrations required to achieve the same result.

Some 15 commercial tablet preparations were analysed by NMR. Six of these preparations were also analysed by ultraviolet spectrophotometry for theophylline and titrimetry (using Bromocresol Green as an indicator) for ethylenediamine.[20] The results presented in Table II are in good agreement.

TABLE I.—ANALYSIS OF KNOWN AMINOPHYLLINE MIXTURES BY NMR

No.	t-Butyl alcohol added *mg*	Aminophylline added* *mg*	Theophylline found *mg*	Ethylene-diamine found *mg*	Theophylline, %*	Ethylene-diamine, %*
1	54·3	191·1	164·7	27·0	86·2	14·1
2	54·5	190·5	164·0	28·2	86·1	14·8
3	49·0	191·1	164·9	27·5	86·3	14·4
4	48·9	190·5	165·0	27·6	86·6	14·5
5	26·9	218·0	187·7	31·4	86·1	14·4
6	50·1	214·2	183·1	31·1	85·5	14·5
7	74·3	213·9	185·0	30·2	86·5	14·1
8	48·3	215·9	185·2	30·9	85·8	14·3
9	56·1	190·9	165·7	27·1	86·8	14·2
10	52·9	210·7	183·5	31·0	87·1	14·7
				Average	86·3	14·4
				Standard deviation	0·5	0·2
				Official USP. procedure	85·6	14·3
				Non-aqueous titration procedure	86·8	14·3

* On anhydrous basis. Aminophylline standard contains 4·06% moisture, based on USP determination.

TABLE II.—DETERMINATION OF AMINOPHYLLINE IN COMMERCIAL PREPARATIONS BY NMR

No.	Aminophylline declared dosage *mg/tab*	Theophylline found by NMR *mg/tab*	Aminophylline found by* NMR *mg/tab*	Aminophylline found by* UV *mg/tab*	Ethylenediamine found by NMR *mg/tab*	Ethylenediamine found by Titration *mg/tab*
1	97·2	73·2	92·8	94·1	10·5	10·7
2	194·4	154·4	195·6	196·0	22·8	23·1
3	97·2	79·2	100·3	100·9	13·3	13·2
4	194·4	161·3	204·3	203·5	23·0	23·3
5	97·2	79·3	100·5	101·5	11·4	11·8
6	200·0	166·4	210·8	210·6	25·2	25·7

* Based on theophylline content.

Acknowledgement—The authors are grateful to Dr. Thomas Medwick, Science Advisor, FDA, New York District and Professor of Pharmaceutical Chemistry, College of Pharmacy, Rutgers University, New Brunswick, New Jersey, for many valuable discussions and encouragement in the preparation of this manuscript.

Zusammenfassung—Es wird ein NMR-Verfahren beschrieben, mit dem Theophyllin und Äthylendiamin gleichzeitig in Aminophyllintabletten bestimmt werden können. Als innerer Standard wurde t-Butylalkohol gewählt, 4% Ammoniak-0,3% Kaliumcyanid in Deuteriumoxid als Lösungsmittel. Das Lösungsmittelsystem wurde so ausgewählt, um mit den Problemen der Löslichkeit von Theophyllin, Überlappung der Resonanzsignale der Komponenten und möglichen Störungen von metallischen Verunreinigungen fertig zu werden. Bekannte Standard- und handelsübliche Präparationen wurden analysiert und die Ergebnisse mit denen anderer Verfahren verglichen. Bei der Anwendung auf die Bestimmung von Aminophyllin in Tabletten geht das Verfahren rasch und einfach; es ist spezifisch und zeigt einen Fehler von 1–2%.

Résumé—On décrit une technique de RMN selon laquelle on dose simultanément la théophylline et l'éthylènediamine dans des comprimés d'aminophylline. On a choisi l'alcool t-butylique comme étalon interne, le solvant étant une solution à 4% d'ammoniaque—0,3% de cyanure de potassium dans l'oxyde de deutérium. Le système de solvant a été sélectionné en envisageant les problèmes de solubilité de la théophylline, le recouvrement des signaux de résonance des composants, et l'interférence potentialle d'impuretés métalliques. On a dosé des étalons connus et des préparations commerciales et les résultats ont été comparés à ceux obtenus par d'autres techniques. La technique, lorsqu'elle est appliquée au dosage de l'aminophylline dans des comprimés, est rapide, simple et spécifique et a une erreur de 1-2%.

REFERENCES

1. F. Reimers, *J. Assoc. Offic. Agr. Chemists*, 1937, **20**, 631.
2. M. Paz Castro and R. Rey Mendoza, *Inform. Quim. Anal.*, 1963, **17**, 158.
3. M. A. Andrade and M. M. L. Inácio, *Rev. Port. Farm.*, 1960, **10**, 141.
4. R. R. Larter, *Australasian J. Pharm.*, 1966, **47**, S33.
5. J. P. Comer and R. B. Bourne, *Drug. Std.*, 1960, **28**, 9.
6. A. L. Glenn, *J. Pharm. Pharmacol.*, 1960, **12**, 595.
7. A. J. Shingler and J. K. Carlton, *Anal. Chem.*, 1959, **31**, 1679.
8. R. Hyatt, *J. Assoc. Offic. Agr. Chemists*, 1954, **37**, 673.
9. A. Bartilucci and C. A. Discher, *J. Am. Pharm. Assoc.*, 1950, **39**, 641.
10. C. Peciar and K. Linek, *Chem. Zvesti*, 1961, **15**, 425.
11. K. Linek, C. Peciar and M. Fedoronko, *ibid.*, 1963, **17**, 510.
12. C. Peciar and K. Linek, *ibid.*, 1961, **15**, 895.
13. M. Sarsunova and J. Tölgyessy, *Z. Anal. Chem.*, 1963, **196**, 107.
14. G. Dušinský and T. Čavaňák, *Cesk. Farm.*, 1958, **7**, 511.
15. T. Yoshino, *Yakugaku Zasshi*, 1958, **78**, 1303.
16. Z. E. Kalinowska, *Acta Polon. Pharm.*, 1964, **21**, 481.
17. C. Runti, *Farmaco (Pavia) Ed. Prat.*, 1956, **11**, 218.
18. M. Plumel, *Ann. Pharm. Franc.*, 1962, **20**, 34.
19. Z. Blagojević, P. Bradić and M. Bunocić, *Schweiz Apoth. Ztg.*, 1960, **98**, 654.
20. T. Medwick and F. Schiesswohl, *J. Pharm. Sci.*, 1963, **52**, 843.
21. M. A. McEniry, *J. Assoc. Offic. Agr. Chemists*, 1957, **40**, 926.
22. P. Kerny, J. P. Billon and F. Bigeard, *Ann. Pharm. Franc.*, 1959, **17**, 284.
23. R. Reiss, *Z. Anal. Chem.*, 1959, **167**, 16.
24. R. Foreman and M. I. Blake, *J. Pharm. Sci.*, 1965, **54**, 12.
25. E. Mutschler and H. Rochelmeyer, *Pharmazie*, 1960 **15**, 582.
26. A. B. Delco and M. J. Stern. *J. Pharm. Sci.*, 1966, **55**, 173.
27. K. Rehse, *Deut. Apotheker-Z.*, 1967, **107**, 1530.
28. *United States Pharmacopeia*, 18th Rev., p. 35. Mack Publishing Co., Easton, Pa., 1970.
29. G. F. Hoffnagle and M. L. Milligan, *J. Am. Pharm. Assoc.*, 1952, **41**, 3.
30. G. B. Griffenhagen and E. S. Brady, *ibid.*, 1951, **40**, 211.

Talanta, 1972 Vol. 19, pp. 1555 to 1561. Pergamon Press. Printed in Northern Ireland

THE DECOMPOSITION OF HYPOBROMITE SOLUTIONS

N. VELGHE and A. CLAEYS
Laboratory of Analytical Chemistry, Faculty of Pharmacy, University of Ghent,
Ghent, Belgium

(*Received* 26 *January* 1972. *Accepted* 30 *March* 1972)

Summary—The stability of 10^{-1}–$10^{-3}N$ hypobromite solutions, stored in brown or colourless bottles at room temperature, has been investigated. A reaction mechanism of decomposition has been proposed and some practical conclusions have been drawn concerning the optimal method of preparation and the required frequency of control of hypobromite solutions used as an analytical reagent.

SEVERAL authors[1–5] have studied the stability of hypobromite solutions during a period of several weeks or months, but most of them did not take account of the formation of BrO_2^- during the decomposition: only the BrO^- concentration and/or the total oxidizing capacity of the solutions are given so the internal composition (content of BrO^-, BrO_2^- and BrO_3^-) remains partially or completely unknown. Only in the study by Hashmi[1] are the concentration-changes of the three oxidizing components followed, but the decomposition curves given by this author show a rather unexpected irregular course.

During a study with hypobromite solutions we worked out an accurate titration method of analysis for the three oxidizing components. In this paper we report use of this procedure to investigate the stability of hypobromite solutions over the concentration range 10^{-1}–$10^{-3}N$.

EXPERIMENTAL

Apparatus

The amperometric titrations were performed with the Metrohm E 261 R polarograph, using a rotating microplatinum-indictor electrode and an Ag/AgCl/satd KCl reference electrode.

Reagents

All reagents were of analytical grade and the water was purified by ion-exchange. Buffer solution with pH 8·3 was obtained by the addition of hydrochloric acid to a borax solution. Standard 0·1*N* arsenite was prepared by dissolving an exactly weighed quantity of arsenious oxide; 0·01 and 0·001*N* arsenite solutions were obtained by dilution.

Solutions of hypobromite. Solutions of about $10^{-1}N$ (indicated as S_1, S_2, S_3) were prepared by addition of 40 ml of 6*N* sulphuric acid to a solution containing 6 g of potassium bromate and 32 g of potassium bromide in 800 ml of water. After a reaction time of one hour 48 ml of 10*M* sodium hydroxide were added quickly (solutions S_1 and S_3) or slowly (solution S_2) and the hypobromite solution obtained was diluted to 2 l. with water.

Solutions, $10^{-2}N$, (indicated as S_4, S_5, S_6) were obtained by tenfold dilution with water of the solutions S_1, S_2 and S_3 respectively.

Solutions, $10^{-3}N$ (indicated as S_7, S_8, S_9) were obtained by hundredfold dilution with 0·01*M* sodium hydroxide of the solutions S_1, S_2, and S_3 respectively.

The pH, measured immediately after preparation, was 12·8 for the $10^{-1}N$ hypobromite solutions and 11·9 for the dilute solutions.

Storage. All the solutions were kept at room temperature (23 ± 1°); the solutions S_1, S_2, S_4, S_5, S_7 and S_8 were stored in brown bottles, the solutions S_3, S_6 and S_9 in colourless bottles. To eliminate the influence of the quality of the glass on stability, identical bottles from the same firm (Scott and Jena) were used after 1 week's pretreatment with $10^{-1}N$ hypobromite.

Determination of the BrO^-, BrO_2^- *and* BrO_3^- *concentration.* A new procedure was used for the determination of the three oxidizing components in the hypobromite solutions. It is based on their reaction with arsenite or iodide at different pH.

Determination of BrO^-. For $10^{-1}N$ solutions, to 25·00 ml of hypobromite solution, 0·1*N* arsenite is added until 1 ml before the equivalence point; after the addition of 25 ml of pH 8·3 buffer and 0·5 ml of 0·05% Bromothymol Blue as indicator, the titration is continued until a colour change from yellow-green to blue-green is obtained.

For 10^{-2}–$10^{-3}N$ solutions, 25·00 ml of hypobromite solution and 10 ml of pH 8·3 buffer are titrated with an equinormal arsenite solution and the equivalence point is detected amperometrically.

Determination of BrO_2^-. For $10^{-1}N$ solutions, 5 ml of 20% potassium iodide solution are added very quickly (addition time <1 sec) to the BrO_2^- solution obtained after the determination of BrO^-; the I_3^- formed is titrated with 0·1*N* arsenite, with starch as indicator. A colour change from mauve to blue-green indicates the equivalence-point.

For 10^{-2}–$10^{-3}N$ solutions, the same procedure is followed as for $10^{-1}N$ solutions but the I_3^- formed is titrated amperometrically with a 0·01 or 0·001*N* arsenite solution.

Determination of total $BrO^- + BrO_2^- + BrO_3^-$. For 10^{-1} *N* solutions, 12 ml of 6*M* hydrochloric acid and 0·5 ml of 0·05% Quinoline Yellow solution are added to 25·00 ml of 0·1*N* arsenite and the solution is titrated with hypobromite until a colour change from yellow to colourless is obtained.

For 10^{-2}–$10^{-3}N$ solutions, 12 ml of 6*M* hydrochloric acid are added to 25·00 ml of 0·01 or 0·001*N* arsenite and the solution is titrated amperometrically with 10^{-2} or $10^{-3}N$ hypobromite.

Calculation of BrO_3^- *concentration.* The concentration of BrO_3^- is obtained by subtracting the sum of the $[BrO^-] + [BrO_2^-]$ from the total oxidizing capacity of $[BrO^-] + [BrO_2^-] + [BrO_3^-]$.

RESULTS AND DISCUSSION

Procedure

The hypobromite solutions (S_1–S_9) were analysed as soon as possible (10–20 min after their preparation) and then after standing during 1, 3 and 6 hr. The analyses were repeated after 24 hr and then at intervals of 3 or 4 days during a period of 29 days; the results of some analyses are summarized in Table I; (*a*), (*b*), (*c*) and (*d*) refer respectively to $[BrO^-]$, $[BrO_2^-]$, $[BrO_3^-]$ and the total $[BrO^-] + [BrO_2^-] + [BrO_3^-]$; the results are expressed in $N \times 10^2$ for the solutions S_1–S_3, $N \times 10^3$ for the solutions S_4–S_6 and $N \times 10^4$ for the solutions S_7–S_9. The $10^{-1}N$ solutions (S_1, S_2, S_3) were further investigated during a total period of 238 days and the results were set out in Figs. 2, 3 and 4.

Initial composition

The analysis during the first hours after preparation demonstrated that after 20 min the internal composition of all hypobromite solutions has already reached an equilibrium and the solutions are ready for use.

The data obtained in the analysis after 1 day (Table I) indicate that the initial internal composition of the hypobromite solutions is dependent on the rate of addition of sodium hydroxide to the acid bromine solution during the preparation: slow addition (S_2) gives a low BrO^- content and a high yield of BrO_2^- and BrO_3^-, while a fast addition (S_1 and S_3) causes a higher BrO^- content, the absence of BrO_2^- and a smaller yield of BrO_3^-. The total oxidizing capacity, however, is not influenced by the rate of addition of alkali.

The effect of varying rate of addition of alkali during the preparation of hypobromite, which was studied in a separate series of experiments, is illustrated in Fig. 1: with slower addition a continuous decrease of BrO^- concentration and increase of BrO_3^- concentration occurs while the BrO_2^- content reaches a plateau with addition times >300 secs. This influence must be attributed to the instability of BrO^-, BrO_2^-, HBrO and $HBrO_2$ in weakly acid and alkaline medium, which

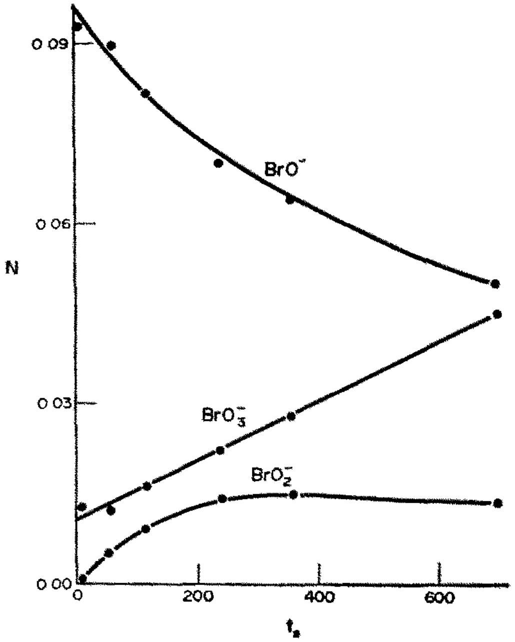


FIG. 1.—Influence of the addition time of NaOH (t_g) on the composition of the hypobromite solution.

results in the partial transformation of these components into the stable BrO_3^- during slow addition of alkali.

Stability of hypobromite solutions

The variation of normality as a function of storage time (Table I) reveals a marked difference between analogous solutions kept in colourless and brown bottles. The variations in concentration of the hypobromite solutions stored in brown bottles (S_1, S_2, S_4, S_5, S_7, S_8) can be explained qualitatively by a decomposition mechanism with two second-order reactions,[6-9] which is supported by the further stability investigation during 238 days:

$$BrO^- + BrO^- \xrightarrow{k_1} BrO_2^- + Br^- \quad \frac{-d[BrO^-]}{dt} = 2k_1[BrO^-]^2 + k_2[BrO^-][BrO_2^-] \tag{1}$$

$$BrO^- + BrO_2^- \xrightarrow{k_2} BrO_3^- + Br^- \quad \frac{d[BrO_2^-]}{dt} = k_1[BrO^-]^2 - k_2[BrO^-][BrO_2^-]$$

$$\times \frac{d[BrO_3^-]}{dt} = k_2[BrO^-][BrO_2^-] \tag{2}$$

In accordance with these reactions the internal composition (concentration of BrO^-, BrO_2^- and BrO_3^-) is more stable for the dilute solutions and the BrO_2^- concentration varies with mode of preparation (S_1 increase; S_2 decrease). The total

Table I.—Decomposition of hypobromite solutions

Solution and component	Storage time, (days)				
	1	8	15	22	29
S_1 *(a)*	9·49	9·35	9·20	9·05	8·93
(b)	0·01	0·12	0·22	0·31	0·42
(c)	1·28	1·29	1·33	1·40	1·39
(d)	10·78	10·76	10·75	10·76	10·74
S_2 *(a)*	5·15	5·07	4·98	4·92	4·85
(b)	1·58	1·53	1·49	1·48	1·45
(c)	4·04	4·16	4·30	4·36	4·47
(d)	10·77	10·76	10·77	10·76	10·77
S_3 *(a)*	9·48	9·30	9·08	8·94	8·76
(b)	0·01	0·10	0·17	0·23	0·28
(c)	1·28	1·34	1·49	1·55	1·68
(d)	10·77	10·74	10·74	10·72	10·72
S_4 *(a)*	9·46	9·43	9·44	9·45	9·41
(b)	0·02	0·02	0·04	0·05	0·04
(c)	1·31	1·32	1·28	1·26	1·30
(d)	10·79	10·77	10·76	10·76	10·75
S_5 *(a)*	5·14	5·12	5·13	5·12	5·10
(b)	1·60	1·59	1·59	1·59	1·58
(c)	4·04	4·08	4·06	4·07	4·10
(d)	10·78	10·79	10·78	10·78	10·78
S_6 *(a)*	9·43	9·26	9·01	8·83	8·57
(b)	0·02	0·02	0·02	0·03	0·02
(c)	1·31	1·44	1·61	1·73	1·94
(d)	10·76	10·72	10·64	10·59	10·53
S_7 *(a)*	9·18	9·16	9·19	9·15	9·13
(b)	0·04	0·03	0·04	0·05	0·06
(c)	1·53	1·48	1·43	1·40	1·38
(d)	10·75	10·67	10·66	10·60	10·57
S_8 *(a)*	4·93	4·97	4·98	4·92	4·87
(b)	1·63	1·60	1·61	1·60	1·60
(c)	4·22	4·16	4·09	4·13	4·15
(d)	10·78	10·73	10·68	10·65	10·62
S_9 *(a)*	8·86	8·07	6·96	5·85	5·00
(b)	0·04	0·04	0·05	0·04	0·04
(c)	1·59	2·03	2·53	3·09	3·38
(d)	10·49	10·14	9·54	8·98	8·42

oxidizing capacity is not influenced by the occurrence of these decomposition reactions; its very slow decrease for the 10^{-1}–$10^{-2}N$ solutions and somewhat more pronounced decrease for the $10^{-3}N$ solutions must be attributed to catalytic reduction[10] or reaction with impurities.

The hypobromite solutions stored in colourless bottles are much less stable than the other solutions: the decomposition rate of BrO^- by transformation into BrO_3^-, and the reduction rate of BrO^-, resulting in a loss of total oxidizing capacity, are both increased by exposure to the light. In contrast to solutions stored in the dark,

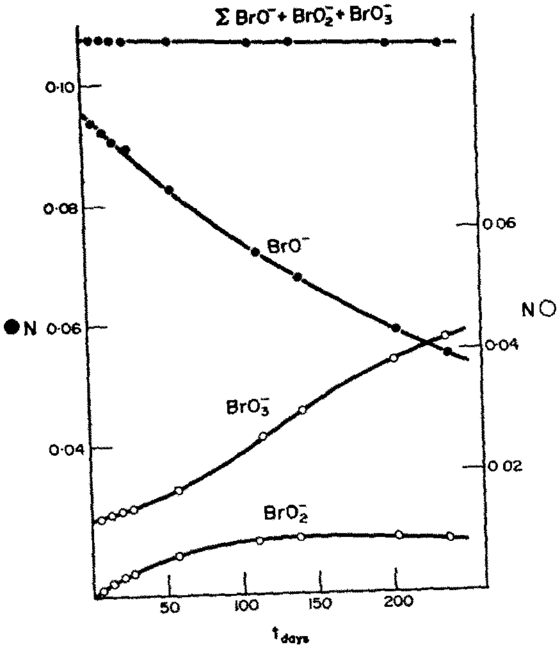


FIG. 2.—Decomposition curves of a BrO_3^--free $10^{-1}N$ hypobromite solution (S_1) stored in a brown bottle.

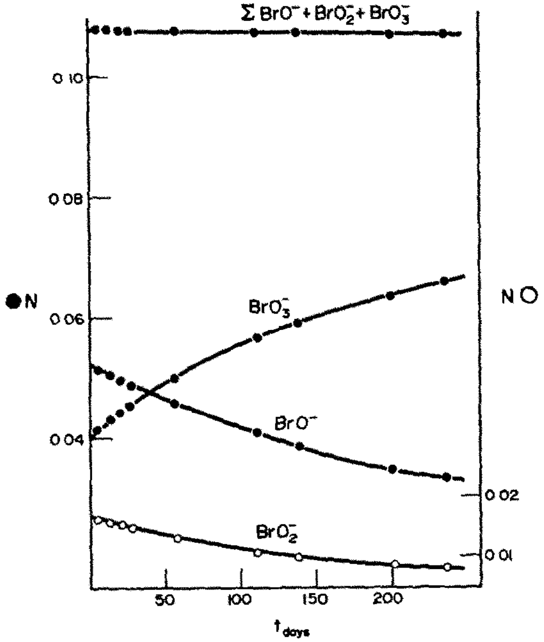


FIG. 3.—Decomposition curves of a BrO_3^--containing $10^{-1}N$ hypobromite solution (S_2) stored in a brown bottle.

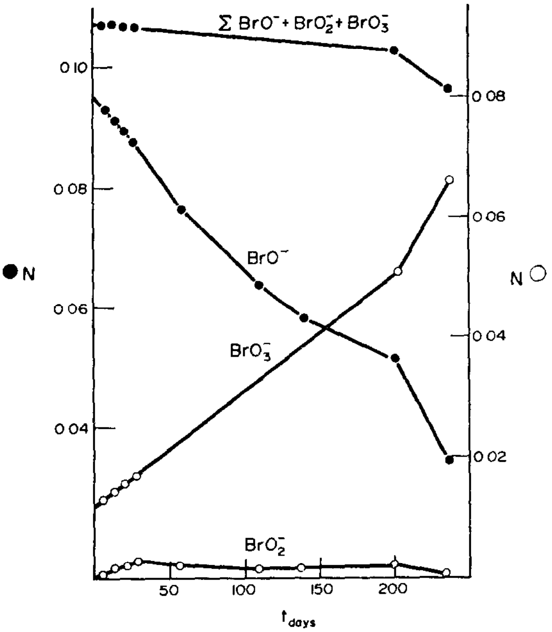


FIG. 4.—Decomposition curves of a BrO_2^--free $10^{-1}N$ hypobromite solution (S_3) stored in a colourless bottle.

in solutions stored in light the total relative variation of BrO^- concentration becomes more pronounced with increasing dilution of the hypobromite solutions.

Stability of $10^{-1}N$ *solutions over a long period*

From the curves of $[BrO^-]$, $[BrO_2^-]$ and $[BrO_3^-]$ as a function of time for the solutions S_1 and S_2 (Figs. 2 and 3) approximate reaction rate constants k_1 and k_2 ($l.mole^{-1}.day^{-1}$) were determined: for solution S_1, $k_1 = 2{\cdot}25 \times 10^{-2}$ and $k_2 = 31{\cdot}1 \times 10^{-2}$, for solution S_2, $k_1 = 2{\cdot}28 \times 10^{-2}$ and $k_2 = 30{\cdot}9 \times 10^{-2}$.

The curves for solution S_3 (Fig. 4) show an irregular pattern which is due to the varying light intensity during the period of storage.

CONCLUSIONS

With the proposed method of preparation, the 10^{-1}–$10^{-3}N$ hypobromite solutions can be used practically immediately after dilution to the required concentration; a maximum yield of BrO^- is obtained by a fast addition of alkali to an acid bromine solution, whereas the total oxidizing capacity $(\Sigma[BrO^-] + [BrO_2^-] + [BrO_3^-])$ is independent of the rate of addition of alkali.

The study of the decomposition of hypobromite solutions demonstrates that storage in the dark is always recommended and becomes an absolute requirement for obtaining sufficient stability of dilute solutions ($<10^{-2}N$). The decomposition of solutions protected from light is caused partly by two second-order reactions which result in a change of the internal composition by the formation of BrO_2^- and BrO_3^- and partly by a reaction with impurities whereby Br^- is formed and the total oxidizing capacity is decreased.

For volumetric applications where $[BrO^-]$ and $\Sigma[BrO^-] + [BrO_2^-] + [BrO_3^-]$ are involved a daily check of the $[BrO^-]$ in $10^{-1}N$ hypobromite is required; a weekly check of this component in 10^{-2}–$10^{-3}N$ hypobromite and of $\Sigma[BrO^-] + [BrO_2^-] + [BrO_3^-]$ in 10^{-1}–$10^{-3}N$ hypobromite is sufficient.

Zusammenfassung—Die Stabilität von Hypobromitlösungen 10^{-1}–$10^{-3}N$, aufbewahrt in braune odere farblose Flaschen, war kontrolliert. Diese Untersuchung erlaubte uns das Reaktionsmechanismus der Zersetzung zu bestimmen und einige praktische Schlüsse zu ziehen hinsichtlich die Optimale Bereitungsmethode und die erforderliche Kontrollefrekwentie von Hypobromitlösungen angewendet als analytisches Reagens.

Résumé—La stabilité de solutions d'hypobromite 10^{-1}–$10^{-3}N$ conservées dans des bouteilles brunes ou incolores a été contrôlée à la température ambiante. Cette étude nous a permis de déterminer les réactions de décomposition, et de tirer quelques conclusions pratiques concernant la méthode optimale de préparation et la fréquence nécessaire de contrôler des solutions d'hypobromite employées comme réactif analytique.

REFERENCES

1. M. H. Hashmi, A. A. Ayaz, A. Rashid and E. Ali, *Anal. Chem.*, 1964, **36**, 1379.
2. M. H. Hashmi, El Ali and M. Umar, *ibid.*, 1962, **34**, 988.
3. H. L. Polak, G. Feenstra and J. Slagman, *Talanta*, 1966, **13**, 715.
4. O. Tomíček and M. Jašek, *Collection Czech. Chem. Commun.*, 1938, **10**, 353.
5. P. Artmann and A. Skrabal, *Z. Anal. Chem.*, 1907, **46**, 5.
6. B. Perlmutter-Hayman and G. Stein, *J. Phys. Chem.*, 1959, **63**, 734.
7. P. Engel, A. Oplatka, B. Perlmutter-Hayman, *J. Am. Chem. Soc.*, 1954, **76**, 2010.
8. R. M. Chaplin, *J. Am. Chem. Soc.*, 1934, **56**, 2211.
9. J. Clarens, *Compt. Rend.*, 1913, **157**, 216.
10. A. A. Sakharov and R. N. Petrovskaya, *Chem. Abstr.*, 1968, **69**, 30514.

Talanta, 1972, Vol. 19, pp. 1563 to 1571. Pergamon Press. Printed in Northern Ireland

QUANTITATIVE REFLECTOMETRY—I

PRINCIPLES AND SCOPE

DAVID KEALEY
School of Chemical Science and Technology, Kingston Polytechnic,
Kingston-upon-Thames, Surrey, U.K.

(*Received* 24 *March* 1972. *Accepted* 25 *April* 1972)

Summary—The technique of quantitative reflectometry is critically investigated, the model being the quantitative determination of nickel in aqueous media. Direct reflectance measurements can be made on commercially available nickel test-strips which develop a pink or red colour in the presence of nickel ions. Relative precisions at the 10 and 50 ppm levels are 2.3-3.6%.

THE DETERMINATION of materials in the form of spots on an absorbent paper or other inert support has been the subject of study for many years. Visual qualitative spot-tests of the type developed by Feigl[1] and his co-workers have provided the basis for many such studies, whilst quantitative aspects of both paper and thin-layer chromatography have been explored in detail. Tananaeff[2] used the term "spot colorimetry" to describe methods of direct measurement, but "reflectometry" is considered more appropriate for the technique described in this paper.

Early attempts to obtain quantitative data directly from spot-tests by reflectance or transmittance measurements yielded relative precisions of 10–20%.[3–8] In some cases, the poor precision can be attributed to variation in spot size, but results were little better when the spots were confined within a pre-determined area.[3,4,6] Malissa[9] considers that poor precision is due primarily to the variable physical properties of absorbent paper and that results achieved by eye are more reliable than those from instrumental measurements. In particular, the ring-oven technique of Weisz[10] has achieved much success, owing to its simplicity, and can give relative precisions of 6–20%. Investigations by other workers[11,12] have shown that large variations occur in detection limits for a number of spot-tests when different sources of filter-paper are used. Ayers[13] has studied spotting techniques and the effect of using different types of filter-paper on the determination of a variety of organic and inorganic species. Although an error of 2–5% was claimed, no details of precision were given. It is apparent that quantitative results obtained by use of conventional spot-test procedures are often unreliable.

Reflectance measurements on spots separated by thin-layer chromatography have yielded relative precisions of 2·2–20%. A bibliography of applications to organic and inorganic systems is given by Frei.[14] However, the overall time for an analysis is usually at least 1–2 hr, and the manipulations involved increase the risk of incurring determinate errors. Vaeck[15] has used a chromatographic technique for the determination of nickel in alloys whereby interfering elements move with the developing solvent, leaving the nickel spot almost at the origin. Uniformity of distribution of nickel over the initial spot area was achieved by applying the spot in 3*M* hydrochloric acid solution. After spraying with rubeanic acid or dimethylglyoxime solution, the reflectance of the dried nickel complex was measured spectrophotometrically. Relative precisions of 1·5–3% were achieved but the complete procedure took 5–6 hr.

The advantages of direct reflectance measurements are speed and simplicity, and the recent commercial availability of reagent-treated test-strips has prompted a fresh examination of this approach. The determination of nickel has been chosen to illustrate the capabilities of the proposed technique as test-strips are available which show a high selectivity for nickel ions. Each strip consists of a white plastic backing (0·55 × 6·0 cm) to which is attached a rectangular piece of white, reagent-impregnated absorbent paper (0·65 × 0·60 cm) close to one end. On immersion in a solution containing nickel ions, the paper becomes coloured from pink to red depending on the concentration of nickel. For semi-quantitative work, a colour-matching chart is provided covering the range 10–500 ppm.

THEORY OF REFLECTANCE MEASUREMENTS

Kubelka-Munk equation

The most widely accepted theory of diffuse reflectance is that developed by Kubelka and Munk.[16] A full account of this theory and the derivation of the basic equation relating reflectance, absorption, scattering and concentration is given by Kortüm.[17] The Kubelka-Munk equation may be written in the form:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \tag{1}$$

where R_∞ is the absolute diffuse reflectance of an infinitely thick opaque layer (in practice 0·1–100 mm depending on particle size), K the absorption coefficient and S the scattering coefficient.

K and S have differing wavelength dependence, hence the equation holds only for monochromatic radiation. For low concentrations of absorbing species on an inert support (diluent) the value of S is determined solely by the diluent and can be assumed to be constant over a limited concentration range. Under such conditions, K is proportional to the concentration of the adsorbed species (*cf.* Beer-Lambert law for solutions) and the equation may be rewritten:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{2{\cdot}303\varepsilon \,.\, C}{S} \tag{2}$$

or

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \text{constant} \times C \tag{3}$$

where ε is the decadic molar absorptivity and C the molar concentration of the adsorbed species.

As in a solution system which obeys the Beer-Lambert law, adherence to this form of the Kubelka-Munk equation is indicated by linearity of a calibration curve. Curvature towards the concentration axis occurs at high concentrations and is attributable to an increasing proportion of regular reflectance.[17] Such reflectance increases with absorption coefficient, K, and particle size, which therefore determine the extent of the linear portion of the curve and the degree of curvature. Other effects may cause curvature at low R_∞ values, and it has been suggested[17] that caution be exercised in using values below 0·6.

The precision of measurements is normally limited to 2–3 % by variations in humidity, but it may well exceed this level, owing to instrumental fluctuations. The variation of relative error with reflectance, assuming a constant instrumental reading error, is similar to that observed for the Beer-Lambert law, *i.e.*

$$\frac{dC}{C} = \frac{(R_\infty + 1)\, dR_\infty}{(R_\infty - 1)R_\infty}$$

When dC/C is plotted as a function of R_∞ (Fig. 1), a minimum occurs at $R_\infty = 0{\cdot}414$. Reflectance measurements outside the range 0·2–0·7 are thus subject to increasingly large instrumental reading errors.

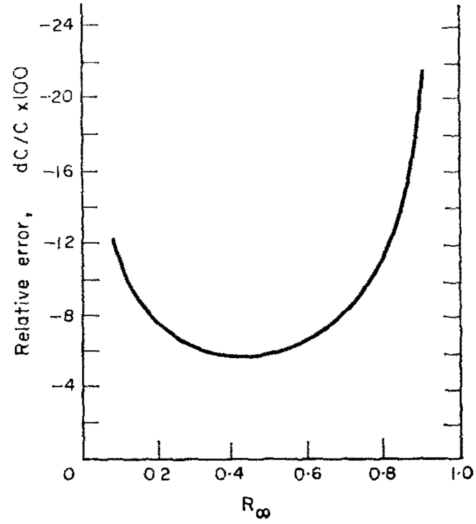


FIG. 1.—Relative error as a function of reflectance, $dR_\infty = 0{\cdot}01$.

It should be emphasized that, like the Beer-Lambert law, the Kubelka-Munk equation represents a limiting case assuming low concentration, monochromatic radiation and a negligible degree of regular reflectance. Strictly, it applies only to absolute reflectance measurements (R_∞) obtained by measuring both samples and blank against an accepted standard of known high reflectance, *e.g.*, freshly prepared magnesium oxide. Only if the diluent or adsorbed species shows very low absorption will a linear curve be obtained by plotting $F(R'_\infty)$ against concentration (R'_∞ represents reflectance measured relative to a blank of the pure diluent). Increasing curvature at low concentrations of adsorbed species will occur, the larger the absorbance of the diluent. For diluents with R_∞ values greater than 0·95 the effect is insignificant.

As an aid to the choice of an optimum concentration range for reflectance measurements, the reflectance values for standards may be plotted as a logarithmic function of concentration (Fig. 2). The curve is similar to a Ringbom plot for solution measurements.[18,19] The linear portion indicates the optimum concentration range and the slope is related to sensitivity and precision. The precision can be calculated for a given instrumental reading error, *e.g.*, for a reading error of 0·01, i.e.; $dR_\infty = 0{\cdot}01$,

$$\frac{dC}{C} . 100 = 2{\cdot}303 \frac{d\,(\log C)}{dR_\infty}$$

or

$$\frac{dC}{C} \cdot 100 = \frac{2{\cdot}303}{\text{slope}}$$

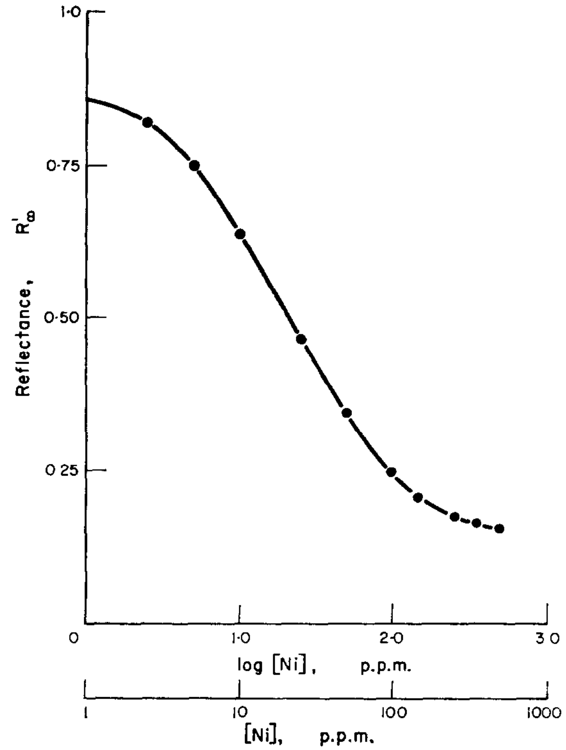


FIG. 2.—Ringbom plot for nickel complex at 547 ± 1 nm. Two-minute immersion time; reference standard MgO.

EXPERIMENTAL

Reagents and apparatus

Standard nickel solution, 500 ppm. Nickel chloride hexahydrate (2·024 g) dissolved in distilled water and diluted to 1 litre. Other standards were prepared by dilution as required.

Nickel test-strips, "Merckoquant," E. Merck.

Magnesium ribbon.

Unicam SP800 recording spectrophotometer.

Unicam SP890 diffuse reflectance attachment.

Joyce-Loebl "Chromoscan" recording densitometer.

Visible reflectance spectrum of the nickel complex

Six test-strips were immersed consecutively in a 10-ppm nickel solution for 2 min (±1 sec), rinsed with distilled water and allowed to dry in air for about 1 hr. The six strips were trimmed to facilitate mounting on a 2½ × 3 in. white card to form a continuous coloured area approximately ¾ × ½ in. The visible reflectance spectrum of the complex was recorded on the SP800 spectrophotometer, with freshly prepared magnesium oxide as a reference standard. Additional sets of six test-strips were prepared and mounted on cards, covering a wide range of nickel concentrations—0, 1, 2·5, 5, 25, 50, 100, 150, 250, 350 and 500 ppm. The period of immersion (2 min), washing and drying procedures were carefully standardized. The reflectance spectrum of each set was recorded as before (Fig. 3).

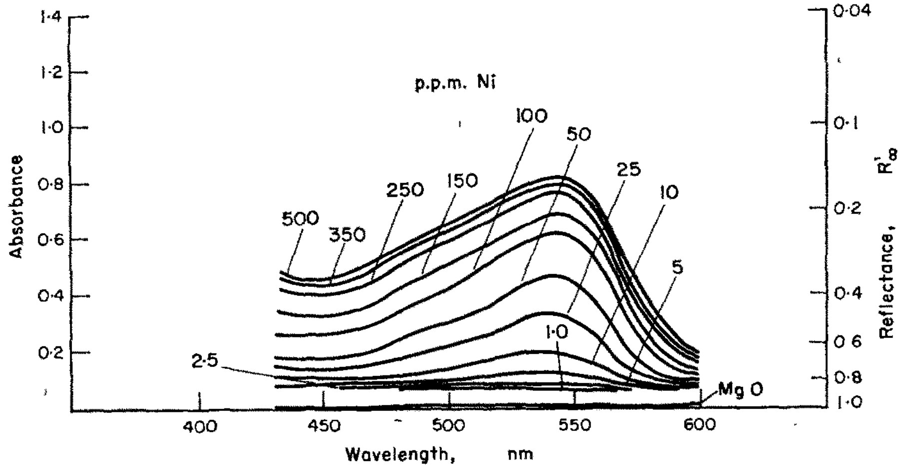


Fig. 3.—Reflectance spectra of nickel test-strips (reference MgO).

Optimization of conditions for quantitative measurements

Reflectance measurements were made on the Joyce-Loebl "Chromoscan," using a green filter (λ_{max} 550 nm), rectangular slit 0510, cams C or D, and neutral density wedge 0-2D. The plastic backing of each strip was trimmed to facilitate mounting at right angles to the direction of scan, and held in position with the white plastic backing plate and elastic sample-retaining strap supplied with the sample holder.

Immersion time. Single test-strips were immersed in 0–100 ppm nickel solutions for times of 0·5, 1·0, 1·5 and 2·0 min (±1 sec), rinsed with distilled water and dried in air for about 1 hr. During immersion, the solutions were gently agitated by hand. Reflectance measurements are given in Table I.

Table I.—Effect of immersion time on reflectance of Ni test-strips

[Ni], *ppm*	Reflectance (cm.)			
	0·5 min*	1·0 min*	1·5 min*	2·0 min*
0	0	0	0	0
10	1·4	1·7	1·85	1·9
25	3·5	4·25	5·4	5·95
50	6·4	7·85	8·15	9·0
75	8·2	10·95	12·6	13·35
100	10·25	12·2	14·2	15·1

Notes 1. Reflectance measured to nearest 0·05 cm.
2. Maximum pen travel is 15·5 cm.
3. 0-ppm (blank) set to zero.
* Immersion time.

Agitation of solutions. Two sets of five test-strips each were immersed consecutively in a 10-ppm nickel solution for 2 min, rinsed with distilled water and dried in air for about 1 hr. For the first set, the solution was agitated gently with a magnetic stirrer; for the second set the solution was not stirred. The procedure was repeated for a 50-ppm solution and reflectance measurements made as before (Table II).

Drying of test-strips. Five test-strips were immersed consecutively in a 10-ppm nickel solution for 2 min, rinsed with distilled water and dried for 3 min with a hot-air blower. The procedure was repeated for a 50-ppm solution and reflectance measurements recorded as before (Table II).

Long-term stability of developed test-strips. Reflectance measurements on a number of test-strips covering the concentration range 0–100 ppm were repeated at intervals over a period of three months (Table III).

TABLE II.—PRECISION OF REFLECTANCE MEASUREMENTS FOR Ni TEST-STRIPS

Conditions		Concentration of Ni, *ppm*	
		10	50
Solution stirred. Strips dried in air for about 1 hr.		5·5	12·2
		5·8	12·7
		5·0	12·0
		5·6	12·6
		5·1	12·5
	Mean	5·5	12·45
	S	0·3$_4$	0·2$_9$
	Relative precision	6·3%	2·4%
Solution not stirred. Strips dried in air for about 1 hr.		3·85	11·6
		3·9	12·1
		3·7	12·5
		3·85	11·85
		4·0	12·15
	Mean	3·86	12·04
	S	0·1$_1$	0·3$_4$
	Relative precision	2·8%	2·8%
Solution not stirred. Strips dried for 3 min with hot-air blower.		3·65	12·05
		4·0	12·55
		3·9	12·1
		3·75	12·0
		3·75	11·8
	Mean	3·81	12·10
	S	0·1$_4$	0·2$_3$
	Relative precision	3·6%	2·3%

Notes 1. Instrument details as in Notes 1–3 in Table I.
2. Variation in blanks <0·1 cm.
3. Estimated standard deviation given by $S = \sqrt{\dfrac{\sum_{1}^{N} (x_i - \bar{x})^2}{N - 1}}$

TABLE III.—VARIATION OF REFLECTANCE OF Ni TEST-STRIPS WITH TIME (MEAN VALUES FOR 5 STRIPS)*

[Ni], *ppm*	Reflectance					S	Relative precision, %
	0†	2†	3†	4†	10†		
10	2·26	2·28	1·95	2·21	2·26	0·1$_4$	6·3
25	4·80	4·74	4·51	4·73	4·31	0·2$_0$	4·4
50	7·26	7·19	6·94	7·10	7·10	0·1$_2$	1·7
75	8·98	8·90	8·64	8·84	8·51	0·1$_9$	2·2
100	10·24	9·94	9·80	9·98	10·01	0·1$_6$	1·6

* Instrument details as in Tables I and II.
† Weeks since preparation.

RESULTS AND DISCUSSION

The visible spectrum of the nickel complex shows a broad maximum at 546 nm which shifts to 548 nm at higher concentrations (Fig. 3), an effect which could be due to an increase in particle size. The system obeys the Kubelka–Munk equation up to 100 ppm of nickel but above this level there is curvature towards the concentration axis (Fig. 4). The onset of curvature would be affected by the quality of the paper and conditions of formation of the complex, both of which affect particle size, which in turn affects the proportion of regular reflectance. Thus, for example, linear response could be extended to higher concentrations by decreasing the immersion time. However, the difficulty in timing short immersion periods accurately would result in poorer precision; one minute is considered to represent a practical lower limit. A Ringbom plot (Fig. 2) confirms that the optimum concentration range, for the conditions used, has an upper limit of around 100 ppm and that the lower limit is around 5 ppm. The relative precision, calculated from the slope of the curve, is 2·8 %, assuming an instrumental reading error of 0·5 %, and 5·6 % for a reading error of 1 %. Measurements need not be restricted to the linear portions of the Kubelka–Munk or Ringbom curves, but results will be less reliable and precision poorer outside these limits. In addition, Fig. 1 demonstrates the importance of restricting reflectance measurements to within the range 0·2–0·7 to minimize instrumental error. The linear portion of the Ringbom curve falls within these limits.

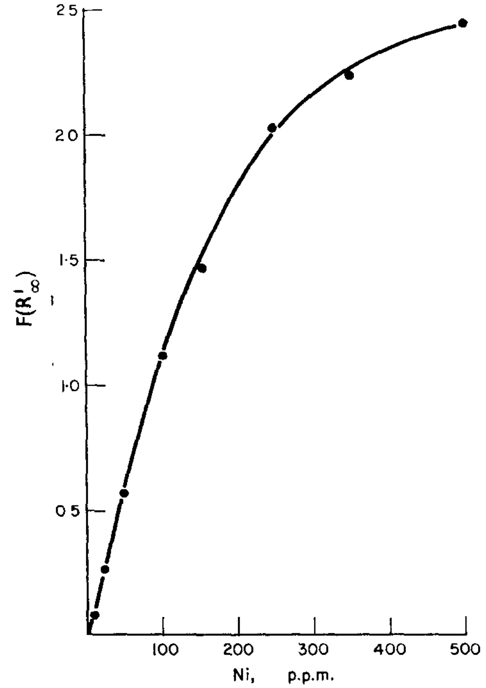


FIG. 4.—Kubelka–Munk plot for nickel complex at 547 ± 1 nm. Two-minute immersion time; reference standard MgO.

Optimum conditions for the preparation of strips for quantitative measurement were established, using the Joyce–Loebl "Chromoscan", a double-beam instrument giving a repeatability of better than 1 %. Measurements can be made on single test-strips, whereas six strips were required to give adequate response on the SP800 spectrophotometer. The spots were scanned across the width of a strip, with a rectangular slit having an area (0·05 cm^2) about 1/7 that of the test area. The recorder trace thus represents the average reflectance from areas equivalent to that of the slit.

Typical traces are shown in Fig. 5. A pronounced edge effect can be observed, owing to a higher concentration of the nickel complex around the edges of the test-strips. Uneven distribution of the adsorbed species is inherent in this type of system because of enhanced capillary flow near the exposed edges of the paper. The average reflectance over the centre two-thirds of the recorder trace is assessed subjectively as shown by the broken lines in Fig. 5. Readings are in arbitrary units, as the design of the instrument does not permit a calibrated response in reflectance. However, scale expansion facilities using cams enable linear calibration curves to be prepared even when the Kubelka–Munk equation is not valid.

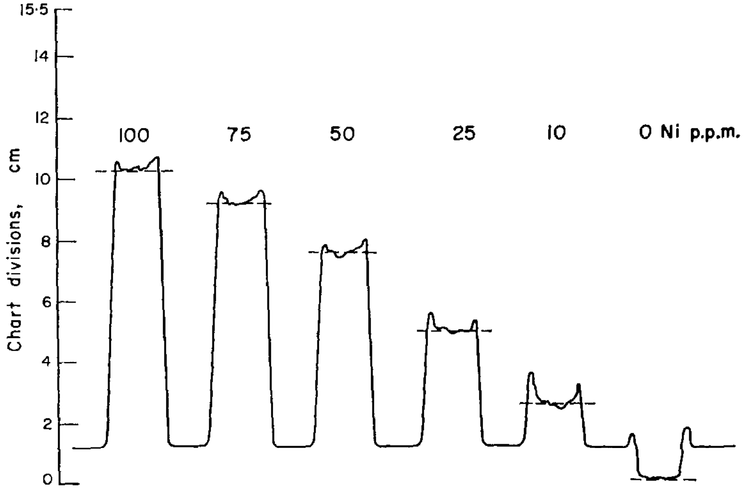


FIG. 5.—Scanning densitometer traces of reflectance of nickel test-strips, at 550 nm.

A 2-min immersion time was selected so as to produce reflectance readings within the optimum range and without incurring significant timing errors. Immersion of the strips in unstirred solutions gave a more even distribution of the complex than did use of continuous stirring. This was particularly noticeable at the 10-ppm level and resulted in poorer precision (Table II). At the 50-ppm level, uneven distribution was again noticeable and the good precision is considered to be fortuitous. No significant differences were observed between those strips which were dried in air for 1 hr and others which were dried with a hot-air blower for 3 min (Table II). Relative precision for unstirred solutions is between 2·3 and 3·6%, which agrees well with the value of 2·8% calculated from the Ringbom curve, for a 0·5% reading error.

The stability of strips covering the concentration range 10–100 ppm, with respect to changes in reflectance over a period of several months, is good (Table II). Relative precision is comparable to that for sets of freshly prepared standards. The variation observed is thought to be due primarily to changes in humidity. Further checks will be made on these particular strips from time to time to assess stability over a longer period.

CONCLUSIONS

It has been shown that quantitative information can be obtained by direct reflectometry using commercially available test-strips for nickel. Relative precision for sets of five standards at the 10- and 50-ppm levels is between 2·3 and 3·6%.

The overall time for the procedure is under 10 min and the long-term stability of prepared standards allows instrument calibration checks to be made very rapidly.

As test-strips for other species in solution become available, it should be possible to develop similar quantitative procedures. Direct reflectometry as described in this paper should be capable of further refinement and it is hoped that it may eventually become a satisfactory alternative to some of the well-established methods of quantitative trace analysis.

Acknowledgement—I should like to express my gratitude to Professor E. J. Shellard of Chelsea College of Science and Technology for the use of the Joyce-Loebl "Chromoscan."

Zusammenfassung—Das Verfahren der quantitativen Reflektometrie wird kritisch untersucht; als Modell wird die quantitative Bestimmung von Nickel in wäßrigen Medien verwendet. An käuflichen Nickel-Teststreifen können direkte Reflexionsmessungen ausgeführt werden: sie zeigen in Gegenwart von Nickelionen eine rosa oder rote Farbe. Die relativen Genauigkeiten bei 10 und 50 ppm sind 2,3-3,6%.

Résumé—On a étudié de manière critique la technique de réflectométrie quantitative, le modèle étant la détermination quantitative du nickel en milieux aqueux. Des mesures de réflectance directes peuvent être faites sur des lamelles réactives de nickel commercialement disponibles, qui développent une coloration rose ou rouge en la présence d'ions nickel. Les précisions relatives aux niveaux de 10 et 50 p.p.m. sont 2,3-3,6%.

REFERENCES

1. F. Feigl, *Qualitative Analysis by Spot Tests*, Elsevier, New York, 1946.
2. N. A. Tananeaff, in F. Feigl, *Tupfelanalyse—Anorganischer Teil*, p. 24, Akadem. Verlag, Frankfurt/Main, 1960.
3. H. Yagoda, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 79.
4. G. P. Skalos, *Mikrochemie*, 1944, **32**, 233.
5. *Idem, Mikrochim. Acta*, 1962, 32.
6. J. H. McCarthy, Jr. and R. E. Stevens, *Anal. Chem.*, 1958, **30**, 535.
7. E. A. Winslow and H. A. Liebhafsky, *ibid.*, 1949, **21**, 1338.
8. P. E. Wenger, D. Monnier and A. Piquet, *Helv. Chim. Acta*, 1946, **29**, 1968.
9. H. Malissa, *From Spot Tests to Spot Colorimetry* in *Analytical Chemistry*, eds. P. W. West, A. M. G. Macdonald and T. S. West, Elsevier, New York, 1963.
10. H. Weisz, *Microanalysis by the Ring Oven Technique*, Pergamon, London, 1961.
11. P. W. West and W. C. Hamilton, *Mikrochemie*, 1951, **38**, 700.
12. G. Ackermann, *Mikrochim. Acta*, 1959, 361.
13. C. W. Ayers, *ibid.*, 1956, 1333.
14. R. W. Frei, *Reflectance Spectroscopy in Thin-Layer Chromatography* in *Progress in Thin-Layer Chromatography and Related Methods*, Vol. II, eds. A. Niederwieser and G. Pataki, Ann Arbor, Michigan, 1971.
15. S. V. Vaeck, *Anal. Chim. Acta*, 1954, **10**, 48.
16. P. Kubelka and F. Munk, *Z. Tech. Physik*, 1931, **12**, 593.
17. G. Kortüm, *Reflectance Spectroscopy*, Springer-Verlag, New York, 1969.
18. A. Ringbom, *Z. Anal. Chem.*, 1939, **115**, 332.
19. G. H. Ayres, *Anal. Chem.*, 1949, **21**, 652.

Talanta, 1972, Vol. 19, pp. 1573 to 1579. Pergamon Press. Printed in Northern Ireland

RAPID SEPARATION AND DETERMINATION OF CHROMIUM

JAMES S. FRITZ and JOHN P. SICKAFOOSE*
Ames Laboratory USAEC and Department of Chemistry, Iowa State University,
Ames, Iowa 50010

(*Received* 16 *March* 1972. *Accepted* 17 *April* 1972)

Summary—Chromium(III) is oxidized to chromium(VI) at room temperature or by conventional persulphate oxidation. The chromium(VI) is separated from other metal ions by retention on a small anion-exchange column, and then eluted with a perchlorate solution and measured spectrophotometrically with a flow-through cell. The method is rapid, selective and amenable to automation.

ADAM AND PŘIBIL[1] have pointed out that direct colorimetric determination of chromate or dichromate, though less sensitive than with the diphenylcarbazide reaction, is more free from interference by other metal ions. These authors used a solvent extraction technique to avoid certain interferences and to achieve concentration of the chromate.

Present anion-exchange separations of chromium(III) are not easily adapted to an instrumental cycle since the resin is not maintained in a single form or the chromium is not retained completely.[2] Chromium(VI) separations[3] require solution conditions for sorption which are difficult to attain after sample dissolution and oxidation.

Recently a forced-flow liquid chromatograph was used for the rapid separation and determination of small amounts of iron.[4] With the aid of a calibration curve, the amount of iron was determined simply by measuring the height of the peak eluted.

This apparatus and principle have now been applied to the determination of chromium. The method described uses strong-base anion-exchange resin in only the perchlorate form to achieve separation from most other metal ions in a short (10-min) analysis cycle for chromium(VI). Solution conditions for sorption and concentration permit use of standard persulphate, periodate or cerium(IV) oxidation procedures. Selectivity of the method for chromium is shown by analysis of National Bureau of Standards samples containing many other metal ions. The detection system uses the absorbance of chromium(VI) at 360 nm to achieve sensitivity in the 1–10 μg range for sample volumes from 40 μl to 5 ml, without amplification of the spectrophotometer signal. A commercial detector with photomultiplier at 254 nm is sensitive to 25 ng of chromium(VI) in the absence of large amounts of nitrate or sulphate.

EXPERIMENTAL

Apparatus

The liquid chromatograph described earlier[4] was used. For a limited number of studies, a Chromatronix Model 200 UV detector was used. This has a 253·7-mm mercury-line source and a 1-cm light-path, 8-μl dead-volume flow-through cell. It is a double-beam differential photometer with a photomultiplier which can be attenuated from 0·01 to 0·12 absorbance units full scale, with a linear dynamic range from 0·0001 to 3·0 absorbance units.

Reagents

Rohm and Haas Amberlyst A-26 strong-base anion-exchange resin was ground wet and sieved while moist, to yield a 140–160 mesh fraction. Approximately 0·5 g of this was slurried with 25 ml of

---

* Present address: Water Analysis Research Laboratory, Hach Chemical Company, Ames, Iowa 50010.

the acidic 0·4*M* sodium perchlorate described below. After 3-min settling the fines were decanted. The decantation procedure was repeated until the supernatant liquid was clear.

A pH-3·75 eluent was prepared by adding perchloric acid to distilled water until the solution reached the required pH, as measured by pH-meter.

The 0·4*M* sodium perchlorate eluent was prepared by acidifying the sodium perchlorate solution to pH 3·75 with perchloric acid.

Ceric ammonium nitrate was dissolved and diluted to volume with 1*M* nitric acid to give a 0·018*M* cerium(IV) solution.

Standard reference materials

The treatment of each sample is described below.

Acid Open-Hearth Steel 20*F*. The sample was dissolved according to a standard procedure,[5] with the minimum necessary amounts of acid. A 20-ml portion of sulphuric–phosphoric acid mixture, (160 ml H_2SO_4 + 80 ml H_3PO_4 per litre) was added and heated. After dissolution, 5 ml of nitric acid were added cautiously and the solution was boiled to remove most of the excess of water and nitric acid. The salts were taken up in 50 ml of 1*M* nitric acid. Silver nitrate solution (2 ml, 1·0% w/v) and 20 ml of freshly prepared ammonium persulphate solution (15% w/v) were added, then the solution was boiled for 20 min, the volume being maintained constant with water. The solution was cooled, diluted to volume with 1*M* nitric acid and analysed within 20 min.

Aluminium Alloy 85*A*. The sample was dissolved according to a standard procedure for non-ferrous alloys,[5] with 10 ml of nitric acid and 2 drops of hydrofluoric acid. Dissolution was slow, so 1 ml of 30% hydrogen peroxide was added dropwise. After complete dissolution, 3 ml of sulphuric acid were added and the solution was evaporated till fuming. Then 25 ml of 1*M* nitric acid, 2 ml of 1% silver nitrate solution and 4 g of ammonium persulphate were added. The solution was boiled for 20 min, the volume being kept constant with water, then was cooled, diluted to volume with 1*M* nitric acid and analysed within 20 min.

Waspaloy (*Ni, Cr, Co*) 349. Dissolution followed the same procedure as for alloy 85A above. The cooled solution was transferred to a volumetric flask, 50 ml of 0·017*M* cerium(IV) in 1*M* nitric acid were added, and the solution was diluted to volume. Oxidation was done 15–20 min before the main analysis.

Standard chromium solution. A 0·05298*M* standard chromium(III) stock solution was prepared by dissolving Baker Analytical Reagent $CrCl_3.6H_2O$ (assay 99·0%) in water and 10 ml of nitric acid. The solution was evaporated to dryness, the residue dissolved in nitric acid and taken to dryness again to remove chloride, the evaporation treatment being repeated a third time. The salts were redissolved and the solution diluted to volume with 1*M* nitric acid. The solution was standardized by the persulphate oxidation method with use of a primary standard potassium dichromate solution and diphenylamine sulphonate indicator instead of permanganate.

Procedure

The 6·3-mm bore analytical column was filled with 0·25 g (weighed dry after use) of 140–160 mesh perchlorate-form Amberlyst A-26 slurried in 0·4*M* sodium perchlorate, pH 3·75. This gave a column bed 1·8 cm long, having a total capacity of approximately 1·5 meq. A typical chromium sample would contain 1×10^{-4} meq of chromium(VI).

The detector was set at 360 nm, with a stray-light filter and a tungsten source. The pressure was set to give a flow-rate of 3·0 ml/min for the acidic 0·4*M* sodium perchlorate eluent used to strip chromium (VI) from the column. The sorbing medium (perchloric acid, pH 3·75) was allowed to pre-equilibrate the column for 2 min before injection of a 0·514-ml sample in approximately 0·5–1*M* nitric acid. After 5·5 min the sample injection valve was returned to the by-pass loop mode to gather another aliquot in the sample loop. At minute 6 the acidic 0·4*M* sodium perchlorate flow was started and chromium was eluted; the peak was obtained within 7 min from the beginning of the chromatography At minute 10 equilibration was started for the next sample.

By means of the peak height obtained, the amount of chromium in the sample was read from a calibration curve prepared with standard solutions by the same procedure.

RESULTS

Oxidation

Cerium(IV) oxidizes[5] chromium(III) to chromium(VI) at room temperature.[6] The chromium(VI) anion is separated from the excess of cerium(IV) on the anion-exchange column. The oxidation of chromium(III) is rapid in dilute perchloric acid, or nitric acid, but slower in sulphuric acid.[7] Nitric acid was chosen for sample dissolution and the oxidation step because chromium(VI) is not retained on the resin from a solution containing enough perchloric acid for the oxidation.

The chromium can be oxidized with in-stream addition of cerium by means of a mixing chamber,[8] provided a delay loop is used to allow sufficient time for the oxidation. Figure 1 shows that 2 min is required for in-stream oxidation of chromium (III) under these conditions.

In the presence of fairly large amounts of manganese(II), cerium(IV) oxidation produces a precipitate of manganese dioxide. For this case and for oxidation of chromium in general, oxidation with persulphate is satisfactory, although it requires heating.

Conditions for separation

Resin. Initially a weak-base anion-exchange resin (Rohm and Haas A-21) was used to permit rapid elution of the chromium(VI) anion with dilute base. However, part of the chromium(VI) was reduced by the resin under the conditions employed. Sussman *et al.*[9] encountered similar difficulty with chromium(VI) on a weak-base anion-exchanger. A macroreticular, strong-base anion-exchanger, Rohm and Haas A-26, was found satisfactory.

Acidity. Chromium(VI) is retained by the A-26 resin in a tight band from 1*M* nitric acid (used in the oxidation step) or from more dilute acid. The ultraviolet spectrum of chromium(VI) changes appreciably with changes in acidity, indicating that a variety of chromium(VI) species is present. In perchlorate media between pH 2 and 4 the spectrum is due solely to $HCrO_4^-$.[10] For this reason, perchloric acid at pH 3·75 was used to equilibrate the column before injection of the sample and to wash ions other than the chromium(VI) anion from the column.

Eluent. Selectivity of the anion-exchange resin in the perchlorate form for chromium(VI) is an important consideration. Except in large concentrations where mass action becomes important, chemical interference is limited to anions of acids, which are stronger than H_2CrO_4 (pK 0·75).[11]

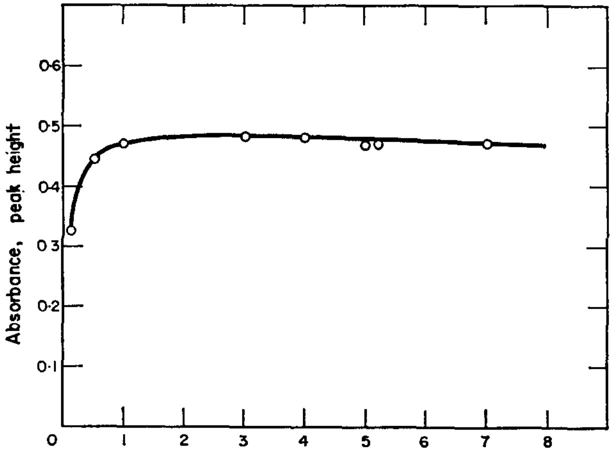


FIG. 1.—Time required for oxidation of chromium(III) by cerium(IV.)
Conditions: 2·08 × $10^{-3}M$ cerium(III) and (IV); 2·97 × $10^{-4}M$ chromium(III) and (VI) in 0·75*M* nitric acid.

The only common mineral acid anion which will rapidly displace chromium(VI) from a strong-base anion-exchange resin at low acidity is perchlorate. Reasons for this extremely high selectivity coefficient of perchlorate have been discussed.[11] A 0·4*M* sodium perchlorate solution adjusted to pH 3·75 with perchloric acid was selected as the lowest concentration able to strip chromium(VI) rapidly from the resin and produce a single coloured species for detection.

Analysis cycle time. The effect of the analysis cycle time on peak height was studied to determine a minimum cycle time. Each phase, pre-equilibration, injection and stripping, was varied in turn while the remaining two were held constant.

Changing the time from sample injection to stripping shows the greatest effect. Peak height decreases as the band spreads by diffusion. An initial change in peak height reflects slow conversion of various chromium(VI) species into a single one.

Detection wavelength. A fixed-wavelength detector at 254 nm with a photomultiplier provides a sensitive method for detecting chromium(VI) in the eluent. In the absence of significant concentrations of nitrate and sulphate, the detection limit, where signal:noise is 2·0, was reached at 25 ng of chromium(VI) in a 5-ml sample, with scale expansion to 0·01 absorbance unit for full-scale deflection.

Because nitrate (0·5–1·0*M* nitric acid) interferes at 254 nm, a wavelength of 360 nm, where it does not, was used. A calibration curve for 360 nm prepared by oxidizing standard chromium(III) solution with cerium(IV) in 5-fold stoichiometric excess is shown in Fig. 2. The deviation of the curve from a straight line at higher concentrations may be the result of the monomer–dimer equibrium of chromium(VI).[12] Curvature at lower concentrations is caused by using peak height rather than area, since the peak base-width remains nearly constant.

Separations

A typical chromatogram is shown in Fig. 3. This figure illustrates the 10-min cycle used for separation of chromium(VI) from a sample. The column equilibrated with perchloric acid (pH 3·75) for 2 min, then the sample is injected. The peaks at about 2·5 min are due to copper(II) and iron(III) in this sample. At minute 6, the

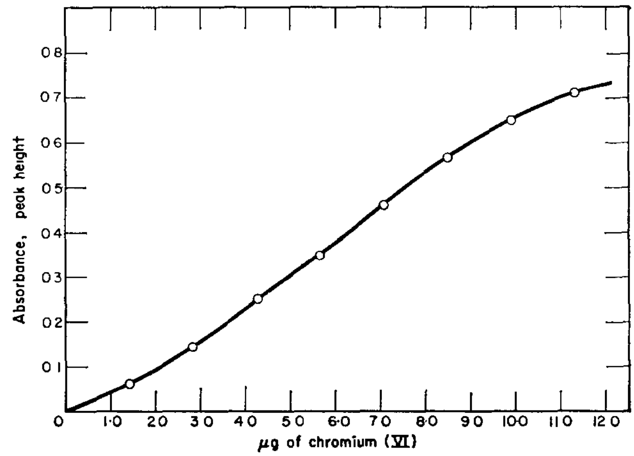


FIG. 2.—Calibration curve for chromium(VI) at 360 nm.

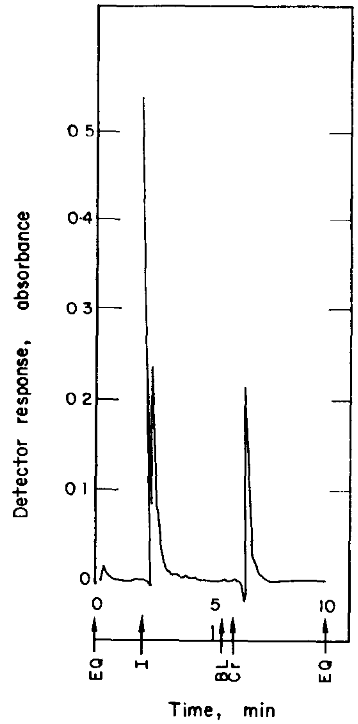


FIG. 3.—Typical chromatogram of chromium analysis.
Conditions: sample NBS 85A, 157·0 mg/50 ml;
0·514-ml loop; detection at 360 nm.

elution of the chromium(VI) is started with acidic 0·4*M* sodium perchlorate; the chromium peak occurs at minute 7. By minute 10 the absorbance has returned to the baseline and the next sample cycle can begin.

Results for analysis of three National Bureau of Standards samples containing chromium are summarized in Table I. In each case the weight of sample taken for analysis was varied so that a 0·514-ml loop containing the appropriate amount of chromium could be used for the calibration curve. Three replicates of each were analysed.

For Alumimium Alloy 85A and Acid Open-Hearth Steel 20F the precision is comparable to that shown on the Certificate of Analysis. Precision for Waspaloy 349 was not indicated by the Provisional Certificate of Analysis with the sample. For steel analysis the result was 4% relative higher than that of the Certificate or 2% relative higher than that of the NBS analyst. Interference studies indicate that this is due

TABLE I.—RESULTS FOR ANALYSIS OF NATIONAL BUREAU OF STANDARDS CHROMIUM SAMPLES

Sample type	NBS No.	Oxidant	NBS analysis, %Cr	Our analysis, %Cr	Std. devn. %Cr	Relative std. devn. %
Acid Open Hearth Steel	20F	$(NH_4)_2S_2O_8$	0·097	0·101	0·0021	2·1
Aluminium Alloy	85A	$(NH_4)_2S_2O_8$	0·231	0·232	0·0055	2·4
Waspalow (Ni, Cr, Co)	349	Ce(IV)	19·50	19·47	0·308	1·6

to the excess of permanganate over chromium(VI). No attempt was made to reduce this selectively with hydrochloric acid as in the titrimetric procedure.

Oxidation of chromium(III) with cerium(IV) in standard sample preparation was used only with Waspaloy 349. For the other samples containing manganese in much larger amounts than chromium, a precipitate of manganese dioxide formed. Although the solution was filtered, chromium results were low. Oxidation with ammonium persulphate proved satisfactory.

TABLE II.—NATIONAL BUREAU OF STANDARDS CERTIFICATE OF ANALYSIS FOR CHROMIUM SAMPLES

Element	NBS 20F, %	NBS 85A, %	NBS 349, %
Cr	0·097	0·231	19·50
Al		Matrix	1·23
B			0·0046
Ca		0·01	
Co			13·95
Cu	0·238	2·48	0·006
Fe	Matrix	0·208	0·13
Ga		0·01	
Pb		0·002	
Mg		1·58	
Mn	0·754	0·66	0·43
Mo	0·058		4·04
Ni	0·243	0·41	57·15
Nb			<0·01
P	0·028		0·002
Si	0·299	0·114	0·29
S	0·034		
Sn	0·021	<0·001	
Ta			<0·01
Ti		0·016	3·05
V	0·007	0·001	
W			<0·01
Zn		0·019	
Zr			0·081

Specificity of this procedure for chromium(VI) is indicated by the elemental analysis of the NBS samples shown in Table II. In a nitric acid sample, elements forming strong nitrate complexes show chemical (column overloading) interference. In nitric acid $<1M$ these are limited to molybdenum(VI), palladium(II), rhenium(VII), gold(III), mercury(II), thallium(I), bismuth(III), neptunium(IV) and plutonium(IV).[13] Another anion interfering chemically is permanganate. Permanganate was retained in a highly coloured band by the column in standard sample analysis and was desorbed only by repeated injections of perchloric acid (1 + 1) into the stripping eluent. No detrimental effect on the resin was apparent.

Zusammenfassung—Chrom(III) wird bei Raumtemperatur oder mit der üblichen Persulfatmethode zu Chrom(VI) oxidiert. Das Chrom(VI) wird durch Adsorption an einer kleinen Anionenaustausch-Säule von anderen Metallionen getrennt, mit einer Perchloratlösung eluiert und spektrophotometrisch in einer. Durchflußzelle gemessen. Das Verfahren ist rasch, selektiv und für die Automatisierung geeignet.

Résumé—Le chrome(III) est oxydé en chrome(VI) à température ambiante ou par oxydation habituelle au persulfate. Le chrome(VI) est séparé des autres ions métalliques par rétention sur une petite

colonne échangeuse d'anions, puis élué avec une solution de perchlorate et mesuré spectrophotométriquement avec une cellule à écoulement continu. La méthode est rapide, sélective, et peut être rendue automatique.

REFERENCES

1. J. Adam and R. Přibil, *Talanta*, 1971, **18**, 91.
2. O. Samuelson, *Svensk Kem. Tidskr.*, 1940, **52**, 115.
3. A. Iguchi, *Sci. Papers Coll. Gen. Educ., Univ. Tokyo*, 1958, **8**, 145, *Chem. Abstr.*, 1959, **53**, 16644.
4. M. D. Seymour, J. P. Sickafoose and J. S. Fritz, *Anal. Chem.*, 1971, **43**, 1734.
5. F. J. Welcher, ed., *Standard Methods of Chemical Analysis*, 6th Ed., Vol. IIA, Van Nostrand, New York, 1963.
6. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1929, **51**, 139.
7. J. Y. Tong and E. L. King, *ibid.*, 1960, **82**, 3805.
8. J. P. Sickafoose and J. S. Fritz, Paper No. 139 presented at the Pittsburgh Conference, March 1972.
9. S. Sussman, F. C. Machod and W. Wood, *Ind. Eng. Chem.*, 1954, **37**, 618.
10. G. P. Haight, Jr., C. C. Richardson and N. H. Coburn, *Inorg. Chem.*, 1964, **3**, 1777.
11. B. Chu, D. C. Whitney and R. M. Diamond, *J. Inorg. Nucl. Chem.*, 1962, **24**, 1405.
12. J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, 1953, **75**, 6180.
13. J. P. Faris and R. F. Buchanan, *Anal. Chem.*, 1964, **36**, 1158.

Talanta, 1972, Vol. 19, pp. 1581 to 1598. Pergamon Press. Printed in Northern Ireland

REVIEW OF THE ANALYTICAL CHEMISTRY OF MELATONIN

E. R. COLE and G. CRANK
Department of Applied Organic Chemistry, The University of New South Wales,
Kensington, 2033, N.S.W., Australia

(*Received* 23 *February* 1972. *Accepted* 28 *April* 1972)

Summary—A survey has been made of procedures, chemical and biochemical, for the separation and estimation of melatonin, the active constituent of the pineal gland. In view of the extremely small amounts of material generally present, discussion is built around chromatographic and spectroscopic techniques leading to a comparison with assays based on the skin-blanching effect of the hormone.

THE INDOLE DERIVATIVE melatonin (*N*-acetyl-5-methoxytryptamine, II in Fig. 1) has been characterized as the active constituent (hormone) of the pineal gland, a small conelike structure situated between the cerebral hemispheres of the mammalian brain. Until recently actions attributable to the pineal gland have been little understood, but a considerable volume of information on its function is now being accrued, including discussions on the relationships between age and weight of the gland and malignancy,[1] as well as on the use of melatonin as an adjunct in the treatment of rhabdomyo- and of osteogenic sarcomas,[2] thus lending interest to the establishment of adequate methods of analysis.

It has been known for over fifty years that mammalian pineal tissue contains a substance extremely potent in effecting blanching of amphibian and fish melanocyte tissue.[3,4,5] An aqueous extract of (50,000) lyophilized beef pineal glands, when submitted to selective extraction by ethyl acetate followed by countercurrent treatment of a concentrate, gave 40 μg of a pure active constituent, the structure of which (II) was suggested by a combination of spectroscopic evidence, chromatographic behaviour and reasoned deduction from comparisons of biological activity with that of other derivatives.[6] The structure was later confirmed by comparison with synthetic material.[7,8]

In considering the problems of its determination it is important to recognize that melatonin is only one of a series of indole derivatives present, which include serotonin (5-hydroxytryptamine, I)[9,10] 5- hydroxy- and 5-methoxyindole-3-acetic acids (III and IV respectively)[11,12] together with 5-methoxytryptophol (V).[13] The inter-relation of these materials is shown by the schematic representation in Fig. 1, in which the sequences leading to the formation of melatonin should be observed.

It was noted that the extract of pineal glands, in preventing the darkening of frog skin by the melanocyte-stimulating hormone, was at least 60 times as active as adrenaline or noradrenaline, 200 times as active as tri-iodothyronine and 5000 times as active as serotonin, thus reinforcing the need for specific characterization and methods of estimation. The scale of the analytical problem in this field is shown by the fact that based on the hydroxyindole-*O*-methyl transferase (HIOMT) activity of pineal tissue, it has been calculated that the output of the metabolite, 6-hydroxymelatonin, would be less than 7 μg per day.[14]

Melatonin is only very slightly soluble in water but is readily soluble in most

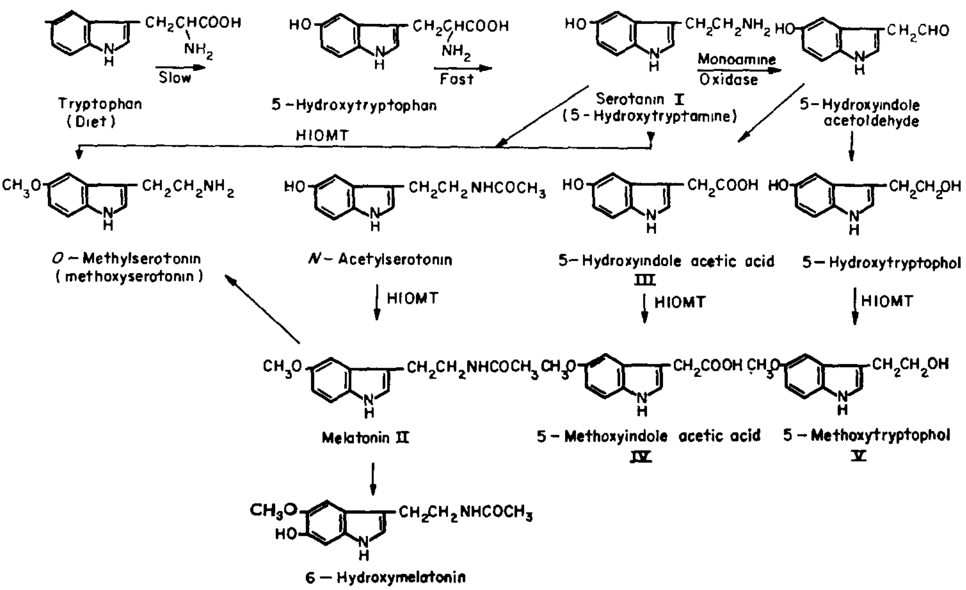


FIG. 1.—Inter-relation of pineal indoleamines and derivatives.

organic solvents and consequently may be extracted from biological materials by ethanol, acetone, chloroform or ethyl acetate. It has recently been found[15] that recoveries of more than 80% may be achieved from serum, either by direct extraction with ether or by continuous extraction with ethyl acetate. Such procedures will remove other indoles plus a great variety of materials normally present in serum. Thus it has been claimed that melatonin, which is chemically neutral, may be separated from acidic and basic substances by suitable treatment with dilute alkali and acid respectively.[16] However, these procedures must be treated with care if melatonin at the microgram level is not to be lost.

CHROMATOGRAPHIC PROCEDURES

In view of the small quantities to be determined it has been inevitable that chromatographic techniques have been well investigated as final steps in separation and estimation procedures.

Paper and thin-layer chromatography

Structural solute/solvent relationships are illustrated in the design of systems for these techniques. Thus in accordance with the polar properties of the solute, higher R_F values are obtained with polar organic solvents, alcohols, chloroform or ether, than with non-polar hydrocarbons (Table I).

It will be seen that addition of water to alcoholic solvents, acidic or basic, is necessary to reduce R_F values to a useful range. Sensitivity of detection on paper chromatograms is about 0·5 μg.

A comparison has been made of the R_F values of melatonin and serotonin with those of other indoleamines of biological origin.[19]

Some attention has recently been given[15] to reversed-phase chromatography in attempts to provide a system with a greater spread of R_F values over the series of

TABLE I.—PAPER CHROMATOGRAPHY OF MELATONIN

Solvent systems	Proportions	R_F for melatonin	Remarks	Refs.
1. *Alcohols*				
(*a*) acidic mixtures				
n-butanol–acetic acid–water	4:1:5	0.87		6, 7, 17
		0.89	High R_F value allows separation from 5-methoxytryptamines and hydroxyindoles	
		0.90		18
	12:3:5	0.90	Note no effect produced with reduced proportion of water	19
		0.87	Serotonin 0.49	20
(*b*) basic mixture				
isopropanol–5% ammonia	4:2		Used for separation of metabolites 6-hydroxy glucuronate R_F 0.22, sulphate R_F 0.55	21
isopropanol–ammonia–water	10:1:1	0.86		6
	16:1:3	0.83	Slight change only in R_F with increased amount of water	
n-butanol–acetic acid–water–pyridine	15:5:12:10	0.9		7
2. *Hydrocarbons*				
Heptane–pyridine	7:3	0.1		7
benzene–ethyl acetate–water	20:1:20	0.39		
3. *Aqueous salt solution*				
20% potassium chloride		0.39		20

derivatives. With Whatman No. 1 paper impregnated with liquid paraffin the influence of various mixtures of methyl alcohol and water on R_F values was determined. It became apparent that although the R_F value of melatonin is related to the strength of the methyl alcohol–water mixture, falling as the alcohol content is reduced, nevertheless the system does not lead to good separation from other tryptamine derivatives. The influence of the stationary phase itself, apart from slightly lowering the R_F values with comparable solvents, is somewhat negligible and the control of the system is dominated by the solvent mixture.

Use of isotopes has been applied to the study of tissue metabolites following intravenous injection of (*a*) acetyl-^{3}H, (*b*) 2-^{14}C or (*c*) methoxy-^{14}C labelling of melatonin. With 3-MM paper and isopropanol–5% ammonia, (2:1), as developing solvent, two peaks, R_F values 0·22 and 0·55, were identified as the glucuronate and sulphate conjugates respectively of 6-hydroxymelatonin, accounting for 5% and 70–80% of administered radioactivity.[21] In this experiment an appreciable fraction (12%) of the radioactivity was attributed to an oxidation product (R_F 0·8), later characterized as 6-hydroxymelatonin itself.[23] In addition, 5-methoxyindole-3-acetic acid, accounting for 0·5% of the activity, has been identified by using the n-butanol–acetic acid–water, (4:1:1) system on 1-MM paper.*

---

* This result leads to the alternative that 5-methoxyindole-3-acetic acid found in pineal body arises either by deacetylation of melatonin followed by deamination or by *O*-methylation of 5-hydroxyindole-3-acetic acid, possibly by HIOMT.

It should be noted that the characteristic R_F values of melatonin may be modified on both paper and thin-layer chromatograms when the material is recovered from samples containing lipid material. If the latter is present as in direct solvent extraction, melatonin is held back, leading to formation of streaks rather than spots.[15]

The problem of tracing melatonin administered in animal experiments is enhanced by the fast rate of metabolism as illustrated by the rate of disappearance in the mouse.[21] Thus there will probably be a need for methods for endogenous rather than exogenous melatonin, and a key to the development of these are methods for 6-hydroxymelatonin and its conjugates in human urine.[14]

Silica gel and polyamide have been used in thin-layer chromatography (Table II). The use of silica gel follows normal practice and the application of polyamide is logical in view of the structural features of the substrate. With this technique a variety of organic solvent mixtures has been used but it has been claimed that two-dimensional chromatography is necessary to achieve a specific separation of melatonin. Moreover prior spraying of the thin-layer with 0·5% methanolic ascorbic acid solution is considered to enhance the stability of melatonin during chromatography.[27]

A summary of the chromatography of melatonin relative to a series of (*N*- methylated) tryptamines with one basic and one acidic solvent, has been presented.[20] Lower R_F values were given by the unacetylated amines with the acidic solvent.

Ion-exchange and gel chromatography

These procedures (Table III) have been mainly used as part of clean-up procedures.

The efficiency of Sephadex-25 in separating melatonin from other components of aqueous extracts of pineal glands has been measured against a synthetic mixture consisting of a macromolecule, "blue dextran" (molecular weight about 2×10^6) sodium chloride (representative of a small molecule) and melatonin. Fractions eluted with distilled water were tested for activity in the blanching reaction.[29] Distribution coefficients for the blue dextran and sodium chloride were 0 and 1 respectively, but K_d for melatonin was 2·8 following adsorption due to the indole nucleus. The correspondence of elution volumes in the control with those of the biological samples provides an inferential method of detection of melatonin (Fig. 2).

TABLE II.—THIN-LAYER CHROMATOGRAPHY OF MELATONIN

Adsorbent	Solvent system	Proportions	R_F for melatonin	Remarks	Refs.
Silica gel G	1. Acidic solvents n-butanol–acetic acid–water	12:3:5	0.90	Serotonin R_F 0.70	20, 21
	2. Basic solvents isopropanol–ammonia–water	8:1:1	0.92	Serotonin R_F 0.68	
Silica gel F254	isopropanol–ammonia–ethyl acetate	2:1:7			17
Silica gel G	3. Two-dimensional (*i*) methyl acetate–isopropanol–25% ammonia	9:7:4		Used for separation from sulphate and glucuronate of hydroxymelatonin	14
	chloroform–methanol	7:3			

TABLE II (*Continued*)

	or				
	(*i*) benzene–acetone (*ii*) ethyl acetate	1:1			
	4. Simple organic solvents				
	chloroform–methanol	9:1	0.34	Used in preparation of β-^{14}C melatonin	14
	chloroform–methanol	85:15		Detected decomposition products as additional spots, higher R_F value than melatonin	
Silica gel two-dimensional	(*i*) methyl acetate–isopropanol–25% ammonia	45:35:20	0.85	Used as two-directional system, claimed nearly specific for melatonin, with quantitative recovery; separates from 5-methoxytryptamine, 5-hydroxyindole-3-acetic acid, *N*-acetylserotonin, serotonin	24
	(*ii*) chloroform–methyl alcohol–acetic acid (two rises)	93:7:1	Separation good	Residual acid from the first solvent improves separation of melatonin following use of second solvent. Ascorbic acid included in loading solvent. Detection by spraying with ethanol–hydrochloric acid, followed by oxidation and colour formation on exposure to air	25
	(*iii*) chloroform–acetic acid	95:5	0.16	Prespray with 0.5% ascorbic acid solution as protective agent	
Polyamide	chloroform–ethyl acetate–acetic acid	7:2:1	0.75		26
	chloroform–acetic acid	9:2	0.80		
	ether–acetic acid	9:2	0.81		
	80% formic acid–water	1:2	0.38		

TABLE III.—ION-EXCHANGE AND GEL CHROMATOGRAPHY

System	Solvent	Remarks	Refs.
Dowex 50 WX 2 (hydrogen form)	Eluted by 0.1*M* ammonia in 65% ethanol	Elutes all indoleamines for later paper or thin-layer separation	20
Sephadex G25	Water	Elution volume 70–100 ml in various samples	28, 29
G15	Loaded from aqueous solution, eluted with 0.01*M* sodium chloride adjusted to pH 4 with hydrochloric acid	Elution volumes: tryptamine 115 ml, melatonin 130 ml, 5-methoxytryptamine 148 ml, serotonin 157 ml	30
G10	Elution pattern for metabolites: 0.1*M* hydrochloric acid and 0.02*M* ammonia, separated by small volume of water, are used in that order	Shows differential action from G-25	31
G10 (short column, 17 cm)	Elution with 0.01*M* sodium hydroxide after equilibration with same solvent	Melatonin appears as separate peak for pineal extracts as follows. Peak 1, mixture of 5-hydroxyindole acetic acid, tryptophan, indole acetic acid, 5-methoxyindole acetic acid Peak 2 melatonin Peak 3 5-methoxytryptophol, tryptamine	32
G10 (long column 143 cm)	Pretreated with 0.2*M* pyridine–0.05*M* acetic acid. Equilibrated and eluted with 0.01*M* sodium hydroxide	Position of melatonin confirmed	

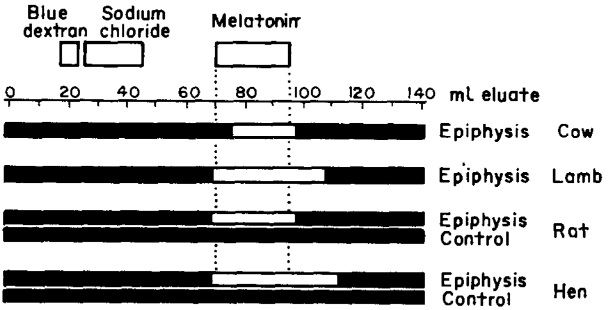


FIG. 2.—Gel chromatography of melatonin. The lower part of the diagram shows the blanching reaction on *Xenopus* larvae (adapted to a black background) after 20 min swimming in the eluate fractions from a Sephadex column. ■ Larvae remain dark: □ Larvae become lighter. The upper part of the diagram shows the elution pattern for the column. (From *Nature*, 1965, **208**, 1324, by permission of the copyright holders.)

Other melanin-concentrating agents which may occur in pineal tissue do not interfere[33,34] and other materials with amine groups—adrenaline, noradrenaline and serotonin—are retarded more on the Sephadex gel owing to its small content of carboxylic acid groups. In effect the gel functions in distilled water as a weak ion-exchange resin.

Gas–liquid chromatography

It is clear that this technique must contend with the polarity and relative involatility of melatonin, leading to the need for high column temperatures (above 200°) and rather long retention times.[35,36] Attention has also been given to control of temperatures (200–250°) at the injection port area, with the observation that for polar compounds subject to strong hydrogen bonding, such as *N*-acetyltryptamine and melatonin, it is necessary to maintain a flash-heater temperature 50–75° above that of the column,[36] otherwise curves assume broad tops suggestive of slow volatilization of the sample.

A balance must be struck between the operating temperature and the level of impregnation with stationary phase. Thus use of SE-30, silicone polymer, at the 0·75% level on silaned Gas Chrom P, was less satisfactory with melatonin than with alkaloids and steroids, despite the lower volatility of these compounds. Better results were obtained with melatonin following column loading at the 4% level but higher column temperatures were then needed.[36] The use of silaned support follows from the need to reduce to a minimum any adsorptive reactions between the compound and support.

It has been claimed that a two-component mixed stationary phase of moderate polar character gives, with a series of catecholamines, tryptamines and other biological amines, symmetrical peaks suitable for quantitative work. The process is aided by the stability of acetyl derivatives, differences in retention times of which are further induced by substitution at the 5-position by methoxyl or acetoxyl. Well-defined separation of *N*-acetyltryptamine, melatonin and diacetylserotonin may thus be attained at 216° on a silicone oil F-60/EGGS column as indicated in Table IV.[34,35]

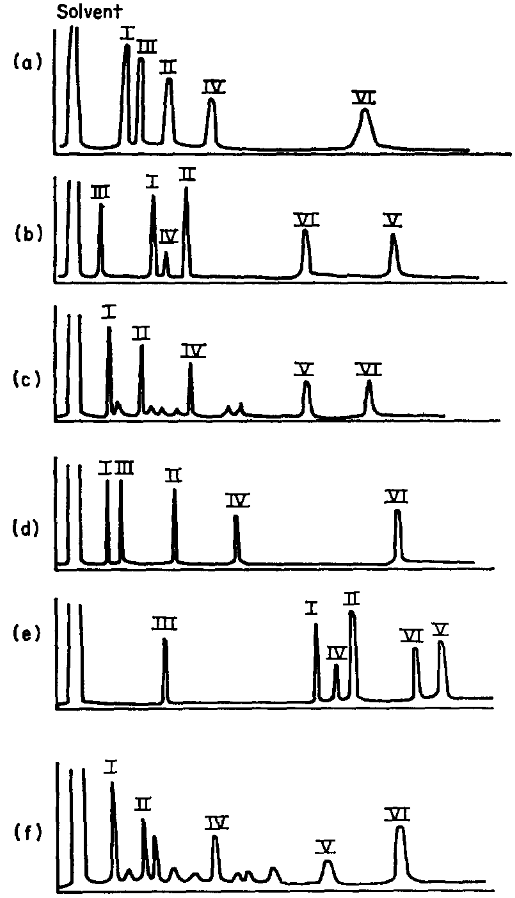
An extensive study of the silyl and trifluoroacetyl derivatives of melatonin and a series of related indoles has shown that relative retention times may be reduced even at considerably lower column temperatures[37] (Fig. 3). Thus clear separation of indoles was achieved in programmed chromatography starting with column temperatures as low as 160°. Conversion into trifluoroacetyl derivatives permits the mildest conditions with longer isothermal periods at lower temperatures. However, the method suffers at present from the fact that several small interfering peaks are obtained from each original indole. The possibility thus exists of interference if the melatonin is present in mixtures although this is not likely to be a common situation.

Limitations are imposed on the use of gas–liquid chromatography in dealing with the ultramicro quantities of melatonin found in body tissues, by the fact that generally only a fraction of a final solution is used for a single determination. Thus the method, even though the most sensitive of the chromatographic methods, is not as sensitive as the fluorometric or bioassay methods.

Where more concentrated solutions of melatonin are used, as in studies of the effect of γ-radiation, gas–liquid chromatography has been useful in showing that four decomposition products are obtained.[38]

TABLE IV.—GAS-LIQUID CHROMATOGRAPHY OF MELATONIN

System	Operating conditions	Retention times	Remarks	Refs.
Silicone oil F-60, 7% with polymer EGGS-2, 1%, on Gas Chrom P support acid-washed and heated with dichlorodimethylsilane	Column temperature 216°	Melatonin approx. 36 min *N*-acetyltryptamine 15 min Diacetylserotonin 85 min	Study incidental to general work on catecholamines and tryptamines, two-component mixed stationary phases	35
Silicone oil DC-W98 10% on Gas Chrom P	Column temperature 265° with injection temperature 250°	Melatonin 3 min	Injection temperature 250°	22
Silicone SE-30, 0.75–4% on acid-washed Gas Chrom P	Support treated with dichlorodimethylsilane, column temperatures varied	Melatonin 28 min at 160°, 24 min at 205°	Used with flash heater zone at 200–250°	35



I = Tryptamine
II = 5-Methoxytryptamine
III = N,N-Dimethyltryptamine
IV = Bufotenin
V = Serotonin
VI = Melatonin

FIG. 3.—Gas-liquid chromatograms of indoles. *a*, *b*, *c*: Isothermal separations of indoles at 220°, silyl derivatives at 200° and trifluoroacetyl derivatives at 180°, respectively. *d*, *e*, *f*: Temperature-programmed separations of indoles, silyl derivatives and trifluoroacetyl derivatives respectively. (Initial temperatures: *d* 180°, *e*, *f* 160°; isothermal period: *d* 6 min, *e* 4 min, *f* 8 min; heating rates: *d* 15°/min, *e*, *f* 10°/min; final temperatures: *d*, *e* 240°, *f* 190°) (From *J. Chromatog.*, 1971, **61**, 225, by permission of the copyright holders.)

COLORIMETRY AND FLUORIMETRY

Colour tests

Colour-developing reagents for the detection of melatonin on paper and thin-layer chromatograms have been related to the presence of the indole nucleus in the molecule.

Ehrlich reagent. The active constituent of this reagent is *p*-dimethylaminobenzaldehyde in mixtures of hydrochloric acid and acetone or ethanol. The reagent gives a blue colour with melatonin, but as a general test for indoles is non-specific for the pineal hormone. The colour with indoles is often purplish at first, turning blue on standing. Colour development is said to be faster after exposure of sprayed thin-layer plates to long-wavelength ultraviolet light. Provided excessive exposure is avoided, improved sensitivity also results.[22] Alternatively brief exposure to vapours from *aqua regia* gives a blue colour almost immediately.[24]

Different formulations are given for Ehrlich's reagent, probably related to variations in shade and rate of colour development. Thus it seems not improbable that modification of the reagent consisting of a simple solution of *p*-dimethylaminobenzaldehyde in ethanol by inclusion of hydrochloric acid was intended to hasten colour development.[39] Similarly replacement of ethanol with the lower-boiling acetone would lead to a faster concentration of reactants on chromatograms. Indeed following upon consideration of earlier reagents,[40] reduction in hydrochloric acid content and consequent water content, has been suggested to overcome slow colour development.[41]

Substitution effects also impose control on the shade of colour. Tryptophan, tryptamine and *N*-mono- and *N,N*-dialkylamines give red-purple colours, but more strongly blue colours are given by the hydroxy and methoxy derivatives—5-hydroxytryptophan, 5-methoxytryptamine and 5-methoxy-*N,N*-dimethyltryptamine.

p-Dimethylaminocinnamaldehyde. This reagent, which gives colours with indole derivatives similar to those given by the Ehrlich reagent, was introduced as a vinyl analogue of the latter, with the expectation that condensation products would be more intensely coloured owing to the greater conjugation.[42] Colours are similar to those given with the Ehrlich reagent but sensitivity is much greater (× 10). However the penalty paid for this greater sensitivity is loss of selectivity.

Ferric chloride–potassium ferricyanide. Depending on reaction with oxidizable substrates to yield blue spots from the products of the reagent, this test, though useful for detection, could not be regarded as specific for indole derivatives. Nevertheless it is useful in locating different members of a known series of compounds.[26] For instance tryptophan is oxidized by ferric chloride to indole-3-aldehyde with concurrent reduction of the iron salt. The reaction of the ferrous iron with ferricyanide, giving Turnbull's Blue, is the basis of the test.

α-Nitroso-β-naphthol. Consequent to the observation that coloured derivatives result from reaction with phenols, this reagent has been applied to the detection[43] and estimation[44] of tyrosine and more pertinently of serotonin as a hydroxytryptamine.[45] Emphasis has been placed on the phenolic group requirement, noting also that both *ortho*- and at least one of the *meta*- positions must be free.[46]

However, the chemistry of the test earlier considered to require concentrated nitric acid, leading to formation of a nitronaphthol, is vague. Modifications of the original conditions propose the use of dilute acids, hydrochloric or sulphuric, in the presence of a small amount of added nitrite, to give a violet chromophore.[47,48] None of the stated structural requirements is provided by melatonin, hence reaction must then depend on other principles, most likely involving the nitroso groups and the heterocyclic ring.

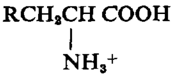
The reagent gives a purple colour with melatonin, deepening over a period of 30 min. Serotonin and its *N*-acetyl derivative give a grey-pink colour changing to grey-violet.[47]

Diazotized sulphanilic acid. This reagent, which may be formed *in situ* by spraying first with a solution of sulphanilic acid in dilute hydrochloric acid, then with sodium nitrite solution, may be used to distinguish 5-hydroxy- from 6-hydroxyindoles. No colour is obtained with serotonin or its *N*-acetyl derivative, contrasting with the brownish red given by 6-hydroxy-*N*-acetyltryptamine. The same colour is given by melatonin despite the absence of a hydroxyl group.[47] The reagent is probably more sensitive than the α-nitroso-β-naphthol reagent.

Fluorimetry

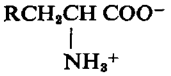
Direct. The ultraviolet absorption curve of melatonin has a peak at 272·5 nm with inflections at 295 and 308 nm. Excitation at about each of these wavelengths has been used as a basis of fluorometric detection and estimation for members of this and related indoles. Emission spectra, subject to control by pH, also contain several peaks. Thus qualitative use has been made of the technique for the identification of serotonin in brain tissue.[49]

With tryptophan as the parent substance, the fluorescence spectrum is determined mainly by the indole ring since various derivatives, indole-3-acetic acid, indole-3-propionic acid, tryptamine and serotonin have practically the same fluorescence as the parent system. Furthermore changes in the pH of solutions of tryptophan, resulting in ionization of the amino or carboxyl groups, have only a weak influence on the position of the band. Thus the three forms **VI**, **VII** and **VIII** have maxima at 347, 353 and 360 nm respectively.[50]



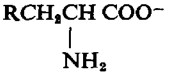
$\mathrm{RCH_2}\underset{\mathrm{NH_3^+}}{\underset{|}{\mathrm{CH}}}\,\mathrm{COOH}$

(VI)



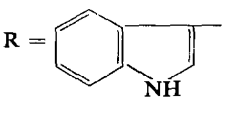
$\mathrm{RCH_2}\underset{\mathrm{NH_3^+}}{\underset{|}{\mathrm{CH}}}\,\mathrm{COO^-}$

(VII)



$\mathrm{RCH_2}\underset{\mathrm{NH_2}}{\underset{|}{\mathrm{CH}}}\,\mathrm{COO^-}$

(VIII)



The simplicity and lack of structure in the fluorescence spectra of indole and tryptophan have been attributed to interaction of the excited state with the surrounding medium.

It is important to note that changes in the fluorescence spectrum occur at very high and very low pH levels. In more strongly alkaline solutions, *e.g.*, 4 % sodium hydroxide solution, the fluorescence curve of tryptophan has a peak in the visible region at 420 nm attributed to ionization of the imino group in the excited state.[50] Quenching effects occur at higher pH levels so that in 4 % sodium hydroxide solution indole and tryptophan exhibit fluorescence with a quantum yield about 1·5 orders of magnitude lower than in neutral solvent. The spectra are often measured in the presence of formaldehyde because in the pH range 11–13 formaldehyde exerts an effective blocking action on the imino group.

These principles have been extended to the tryptamines, including serotonin and melatonin[51] (Table V). Following excitation at 307 nm melatonin gives a fluorescence spectrum with a peak at 430 nm, having an intensity exceeded only by that of 5-methoxytryptamine. Inclusion of formaldehyde gives at 360 nm a peak intensified nearly ten times. Other tryptamines show similar changes under these conditions. It will be seen, however, that the most significant change is produced under the third set of conditions, which leads to peaks in the visible region (545–560 nm) with much lower intensity, and serves to distinguish the 5-hydroxy- and 5-methoxy- derivatives from the other types. Indoles without this substitution in the 5-position show only low fluorescence between 340 and 440 nm. Thus a degree of specificity is introduced with the technique.

Over the pH range 2–11 unsubstituted indoles on excitation at 275 nm give a peak in the fluorescence spectrum at 360 nm. In contrast, excitation of 5-hydroxyindoles at 295 nm leads to a peak at 330 nm. With $3M$ hydrochloric acid as medium, activation at 295 nm and measurement of a peak in the visible region at 540–550 nm provides a specific test for 5-hydroxy- and 5-methoxyindoles. The degree of specificity is indicated by the fact that a series of closely related compounds, tryptophan, 5-methyltryptophan, tryptamine, 3- and 5-methylindole, indole-3-acetic acid, 4-hydroxytryptophan, 4- and 6-hydroxytryptamine, 4-hydroxy-*N*, *N*-dimethyltryptamine-*O*-phosphoryl ester and 6-methoxyindole do not show this characteristic.[52] Thus it is not surprising that with the need for methods for the estimation of ultramicro quantities of 5-hydroxytryptamine and in view of the suggestion that the fluorescence measurement shows more discrimination than the colorimetric and spectrophotometric assays,[45] considerable effort has been applied to putting this technique on a sound basis.[49]

It is important to emphasize the fact that the change in the fluorescence spectrum of these derivatives with change in pH of the medium has itself been used for selective measurements. The shift to 540–550 nm has been particularly useful, illustrated by change in technique applied to serotonin previously measured at 295 nm excitation and 350 nm fluorescence.[49] Limitations remain since 5-methoxy derivatives still have only weak fluorescence and require chromatographic or selective solvent separation for specificity.[53]

Conditions affecting the fluorescence of melatonin in relation to other tryptamines have been examined as a basis of method of assay,[17] with the conclusion that the spectrum, although very similar to those of 5-hydroxyindoles and 5-methoxytryptamines, nevertheless is sufficiently distinctive to be used selectively. Conforming to the general pattern, the spectrum is sensitive to change in pH of the medium. In neutral or weakly acid medium (pH 4) maximum excitation is achieved at about 300 nm, giving a fluorescence peak at 355 nm. These values contrast with those for serotonin (302 nm excitation, 338 nm peak) and for 5-methoxytryptamine (300 and 345 nm) (Fig. 4).

Differences in the spectra of serotonin and melatonin in more strongly acid media are shown in Fig. 5 in which should be noted the appearance of the band at 540 nm for serotonin and at 550 nm for melatonin. The intensity of this band increases with increase in acidity and varies inversely as the band at 355 nm, which is therefore correspondingly lowered as the pH of the solution is lowered.

The intensity of the 355 nm band for melatonin is at its maximum over the pH

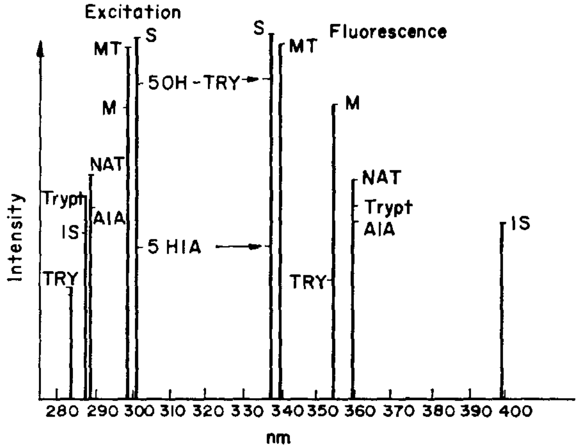


FIG. 4.—Excitation and emission maxima of various indoles at the same concentration and pH (4). M–melatonin; S–serotonin; MT–methoxytryptophan; NAT–*N*-acetyltryptophan; IS–indoxyl sulphate; AIA–indole acetic acid; 5HIA–5-hydroxyindole acetic acid; TRY–trytophan; TRYPT–tryptamine. (From *Clin. Chim. Acta* 1970, **30**, 519, by permission of the copyright holders.)

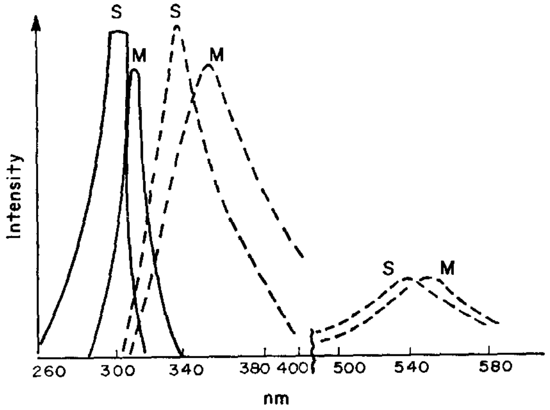


FIG. 5.—Excitation and emission spectra of serotonin and melatonin in 0.1*M* hydrochloric acid. ——— excitation – – – emission S–serotonin; M–melatonin (From *Clin. Chim. Acta*, 1970, **30**, 519, by permission of the copyright holders.)

range 6–10. Differences in degree of response of other tryptamines with change in pH have been observed, leading to various intersections of the curves.

Derivatives—the o-phthalaldehyde reaction. 5-Hydroxy- and 5-methoxytryptamines, with a side-chain of even one carbon at the 3- position, when heated with *o*-phthalaldehyde in acid solution give intensely fluorescent products.[54] The fluorescence given by the various derivatives is similar, with activation maximum at 360 nm and emission maximum at 470 nm. The relative intensity however varies considerably. It will be seen that indole itself does not lead to fluorescence nor does substitution singly with hydroxyl or methoxyl at the 5-position (R_1) or with a side-chain at the 3-position (R_2) lead to a marked increase. By contrast the doubly substituted derivatives (at R_1 and R_2) are much more strongly fluorescent. The necessity for hydroxyl or methoxyl at the 5-position must be emphasized since fluorescence does not follow substitution by methyl despite the presence of a side-chain at the 3-position. Further discussion of structural requirements has appeared.[55,56]

Application of the reaction to the detection of serotonin on thin-layer chromatograms has been tested with a reagent that includes cysteine.[57] Inclusion of the cysteine leads to fluorescence maxima at wavelengths 10 nm longer than those obtained in its absence.[54] Thus although the fluorescence reaction itself is not specific for indolealkylamines substituted at the 5-position, nevertheless the maxima at 470–480 nm appear to make the test specific for this group of compounds.[57] In the present context melatonin gives the greatest response, approached only by the related unacetylated 5-methoxytryptamine (Table V).

The test evolved from a survey of products from the reaction of amino-acids with aromatic aldehydes, earlier considered to involve, partly at least, a Strecker degradation.[58] An equivalent survey of various carbonyl compounds using 5-hydroxytryptamine as reference material, emphasized the specificity given by aromatic 1,2-dialdehydes in the fluorescence reaction. In the acid medium the reaction is specific for tryptamines and interference from a variety of amino-acids such as glycine, histidine, phenylalanine and di-*o*-hydroxyphenylalanine, is removed.

Comparison of the relative intensity of the fluorescence of the 5-hydroxytryptamine–phthalaldehyde product with the native fluorescence of the amine in aqueous solution is shown in Table VI.

BIOASSAY TECHNIQUES

Historically, bioassays of pineal substance preceded the isolation of melatonin as the active constituent, with the demonstration that injections of extracts of pineal bodies into toads (*Xenopus laevis*) led to contraction of melanophores in a specific manner.[59] From such results it was possible to predict that the active component would be relatively stable, since it survived boiling, and of low molecular weight by dialysis for 24 hr in distilled water.

It has been pointed out that although the technique has been used as a screening test to determine presence or absence of melatonin[28,29,60], or as a quantitative assay for relative values in serum,[61] the applications of melatonin bioassay have never been fully exploited.[62] However, the establishment of bioassay procedures may represent a major commitment in terms of laboratory time and facilities, to be justified by the extent of involvement in study of the pineal function and related problems.

The method is highly specific and, as indicated above, more sensitive than the fluorimetric method, since melatonin is more potent by several orders of magnitude than any other known agent in the blanching reaction. Within the frog melanophore, concentrations as low as 1 pg/l. are sufficient to cause aggregation.

Relative potencies in these effects may be alternatively expressed. Based on the use of frog melanocytes, 0·45 μg of melatonin has the same effect as 20 μg of epinephrine or of norepinephrine. Specific structural requirements are illustrated by the fact that serotonin, the melatonin precursor, has no skin-lightening effect in doses up to 4000 μg.[63]

It may also be observed that the skin-lightening action of melatonin, as the active principle of the pineal gland, is opposed to the melanocyte-stimulating hormone of the pituitary gland. Indeed the pineal and pituitary glands have been discussed as functional mirror images of each other.[64]

TABLE V.—RELATIVE FLUORESCENCE INTENSITIES OF 3- AND 5-SUBSTITUTED INDOLES IN THREE SOLVENT SYSTEMS: I, M NaOH; II, 40% FORMALDEHYDE-1M NaOH (1:1); III, 1M NaOH–ACETIC ANHYDRIDE (1:1). CONCENTRATION OF ALL COMPOUNDS $5 \times 10^{-5}M$

Compound	R_3	R_5	I	II	III	
Indole			2.4(400)	20.2(380)	2.1(380)	
Indole-3-carboxylic acid	$-COOH$		13.0(380)	70.6(340)	7.7(360)	
Indole-3-acetic acid	$-CH_2COOH$		11.6(420)	100 (380)	1.9(360)	
Tryptophol	$-CH_2CH_2OH$		7.4(420)	102 (380)	2.7(360)	
Tryptamine	$-CH_2CH_2NH_2$		8.5(420)	158 (370)	3.0(360)	
Tryptophan	$-CH_2CH(COOH)NH_2$		9.0(420)	205 (360)	1.3(360)	
5-Methyltryptophan	$-CH_2CH(COOH)NH_2$	$-CH_3$	11.8(400)	186 (360)	7.1(360)	
N-Aacetyltryptamine	$-CH_2CH_2NHCOCH_3$		9.1(420)	77.3(380)	2.3(360)	
N-Acetyltryptophan	$-CH_2CH(COOH)NHCOCH_3$		6.5(420)	87.6(380)	1.5(340)	
5-Hydroxyindole-3-acetic acid	$-CH_2COOH$	$-OH$	74.4(460)	64.7(380)	8.6(340)	2.3(560)
Serotonin (5-hydroxytryptamine)	$-CH_2CH_2NH_2$	$-OH$	6.2(380)	32.8(380)	9.3(360)	2.2(560)
5-Hydroxytryptophan	$-CH_2CH(COOH)NH_2$	$-OH$	8.0(380)	40.9(380)	8.3(340)	2.1(560)
N-Acetylserotonin	$-CH_2CH_2NHCOCH_3$	$-OH$	9.1(380) 12.6(460)	56.7(380)	13.0(360)	3.4(560)
5-Methoxyindole-3-acetic acid	$-CH_2COOH$	$-OCH_3$	64.9(430)	455 (360)	17.8(340)	28.9(545)
5-Methoxytryptamine	$-CH_2CH_2NH_2$	$-OCH_3$	117 (430)	850 (360)	109 (340)	95.3(545)
Melatonin	$-CH_2CH_2NHCOCH_3$	$-OCH_3$	74.8(430)	672 (360)	81.2(340)	61.0(545)

Values in parentheses represent the fluorescence maximum in nm. Excitation wave-length: 307 nm.
Excitation and emission slit: 1 mm. (From *Experientia*, 1967, **23**, 906, by permission of the copyright holders.)

TABLE VI.—RELATIVE FLUORESCENCE OF 5-HYDROXYTRYPTAMINE UNDER VARIOUS CONDITIONS

	$3M$ HCl	pH 7	Phthalaldehyde reaction
Activation wavelength	295	303	360
Emission wavelength	550	338	470
Reagent blank	2	18	2
5-Hydroxytryptamine (1 μg/ml)	66	550	1390
Fluorescence ratio	33	31	695

(From *Anal. Chem.*, 1966, 38, 1937, by permission of the copyright holders.)

Bioassay procedures have been reviewed[65] and fall mainly into two groups, as follows.

Methods dependent on changes in transmission or reflectance of incident light by isolated frog skin

In the absence of earlier knowledge of the active constituent of the pineal gland considerable attention was given to improvement of assay techniques by measuring light transmitted through frog's skin,[66,68] leading to some simple arrangements of apparatus,[68,69] (*e.g.*, that[69] shown in Fig. 6). Results are expressed as a "unit" of melatonin, which is that quantity producing minimum increase in light transmission. Thus if a solution must be diluted 100,000 times to produce the minimum effect, the sample contains 100,000 units.

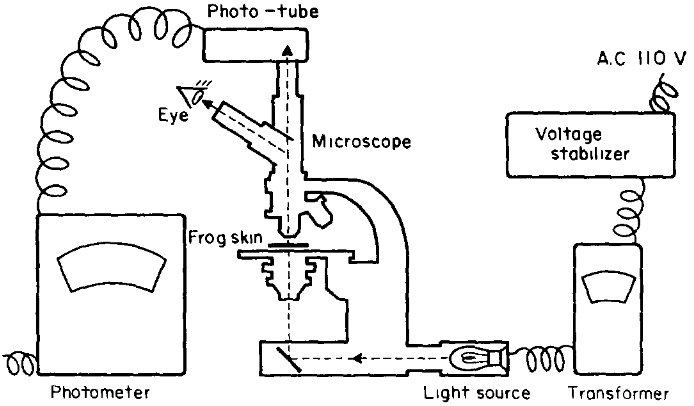


FIG. 6.—A simple arrangement for measuring transmission of light through frog skin. (From *Endocrinol.*, 1960, 67, 443, by permission of the copyright holders.)

With a 10X objective lens 50 melanocytes at a time may be observed but changes in a single cell may be observed with a 75X objective. The technique requires that the population density of melanophores be relatively large and fully dispersed—about fifty cells per field. Few cells other than melanocytes must be present and the skin section must be relatively thin. Best response is given by skin from the median dorsal portion of the thigh. Application to homogenates of rat and hen pineal glands following fractionation on Sephadex G25, has been discussed previously,[29] while detection of melatonin on paper chromatograms has followed transfer of cut sections of the paper to the liquid bathing *Xenopus* larvae.

The method follows development of the concept of a "melanocyte index", employing a microscope for measurement.[70]

Tests on a variety of compounds have confirmed the specificity of this method. A metabolic product, 6-hydroxymelatonin, is about the only other compound to produce an effect at low dose, but its minimum effective dose (MED)—0·1 μg ml—is still considerably higher than that observed for melatonin. Thus the addition of the hydroxyl group in the 6-position raises the MED by a factor of 10^3, clearly demonstrating that essential structural requirements for highest activity are the tryptamine nucleus with 5-methoxyl and *N*-acetyl groups.[71]

Microscopic measurement of degree of melanin dispersion within melanophores—Hogben Index

The Hogben Index has been developed as a measure of the body-lightening reaction as in *Xenopus* larvae.[27]

The dermal melanophore response of larval *Rana pipiens* has been developed as a quantitative method, in which the critical element is rigid attention to details of the test procedure. This is based on a constant supply of perfectly uniform test animals emanating from a tadpole-culturing programme.

The responsiveness of the dermal melanophores to melatonin varies with an endogenous 24-hr rhythm, with light-adapted animals maintained under a specified light regimen appearing optimally responsive at a set period.

Melanophores in a triangular area between the eye and mouth on the left side are "read" in the killed (with formalin) and fixed animal. Measurements are made on a group of ten tadpoles after their immersion for 30 min in the test sample. Reading, on the basis of an estimate of the average state of the melanophores in a field, consists in assigning an appropriate stage number according to the Hogben Index.[72] The mean melanophore stage shown by each group after collation is used to construct a calibration curve plotted on two cycle semi-log paper with melanophore stages represented on the linear axis and melatonin concentrations on the log scale.[62] Between zero and 1 μg/ml a linear relationship is shown but sensitivity lessens at higher concentrations.

This technique has been applied to studies of diurnal variations in pineal melatonin of rats, quail and chickens, including the effect of surgical procedures.

Acknowledgements—The support of this work by the New South Wales State Cancer Council is gratefully acknowledged.

Zusammenfassung—Es wird eine Übersicht über chemische und biochemische Verfahren zur Abtrennung und Bestimmung von Melatonin, dem aktiven Bestandteil der Epiphyse, gegeben. In Anbetracht der normalerweise vorliegenden extrem kleinen Stoffmengen wird die Diskussion auf chromatographischen und spektroskopischen Verfahren aufgebaut; diese werden schließlich mit Analysenmethoden verglichen, die auf der hautbleichenden Wirkung des Hormons beruhen.

Résumé—On a effectué une étude des techniques, chimiques et biochimiques, pour la séparation et le dosage de la mélatione, le constituant actif de la glande pinéale. Eu égard aux quantités extrêmement faibles de produit généralement présentes, la discussion est établie autour des techniques chromatographiques et spectroscopiques menant à une comparaison avec les essais basés sur l'effet de blanchiment de peau de l'hormone.

REFERENCES

1. A. Rodin and J. Overall, *Cancer*, 1967, **20**, 1203.
2. K. W. Starr in *Progress in Clincial Cancer*, Vol. IV, p. 1. Brune and Sutton, New York, 1969.
3. C. P. McCord and F. P. Allen, *J. Exp. Zool.*, 1917, **23**, 207.
4. J. S. Huxley and L. B. Hogben, *Proc. Roy. Soc.*, (*London*), 1922, **B93**, 36.
5. L. Gianferrari, *Arch. Sci. Biol.*, 1922, **3**, 39.
6. A. B. Lerner, J. D. Case, Y. Takahashi and W. Mori, *J. Am. Chem. Soc.*, 1958, **80**, 2587.
7. A. B. Lerner, J. D. Case and R. V. Heinzelman, *ibid.*, 1959, **81**, 6084.
8. J. Szmuskovicz, W. C. Anthony and R. V. Heinzelman, *J. Org. Chem.*, 1960, **28**, 857.
9. N. J. Giarman and M. Day, *Biochem. Pharm.*, 1959, **1**, 235.
10. N. J. Giarman and D. X. Freedman, *Nature*, 1960, **186**, 480.
11. A. B. Lerner, J. D. Case, K. Beirmann, R. V. Heinzelman, J. Szmuskovicz, W. C. Anthony and A. Krivis, *J. Am. Chem. Soc.*, 1959, **81**, 5264.
12. A. B. Lerner, J. D. Case and Y. Takahashi, *J. Biol. Chem.*, 1960, **235**, 1992.
13. R. J. Wurtman and J. Axelrod, *Progr. Brain Res.*, 1965, **10**, 520.
14. R. L. Jones, P. L. McGeer and A. C. Greiner, *Clin. Chim. Acta*, 1969, **26**, 281.
15. E. R. Cole and G. Cranke, unpublished results.
16. R. P. Maickel and F. P. Miller, *Adv. Pharmacol.*, 1968, **6A**, 71.
17. C. Dreux, *Clin. Chim. Acta*, 1969, **23**, 177.
18. J. Supniewski and S. Misztal, *Bull. Acad. Polon. Ser. Sci. Biol.*, 1960, **8**, 479.
19. N. Prop and J. A. Kappers, *Acta Anat.*, 1961, **45**, 90.
20. H. Tanimukai, *J. Chromatog.*, 1967, **30**, 155.
21. I. J. Koplin, C. N. B. Pore, J. Axelrod and H. Weissbach, *J. Biol. Chem.*, 1961, **236**, 3072; *Biochim. Biophys. Acta*, 1960, **40**, 377.
22. J. Pennington, *J. Chromatog.*, 1968, **32**, 406.
23. R. J. Taborsky, P. Delvigs and I. H. Page, *J. Med. Chem.*, 1965, **8**, 855.
24. J. C. Fenwick, *Gen. Comp. Endocrinol.*, 1970, **10**, 86.
25. D. C. Klein and A. Notides, *Anal. Biochem.*, 1969, **31**, 480.
26. K. J. Wong, Y. C. Tung and H. H. Lai, *Nature*, 1967, **213**, 213.
27. W. B. Quay and J. T. Bagnara, *Arch. Int. Pharmacodyn.*, 1964, **150**, 137.
28. F. C. G. van de Veerdonk, *Int. Pigm. Cell Conf. 6th, Sofia*, 1966, p. 82.
29. F. C. G. van de Veerdonk, *Nature*, 1965, **208**, 1324.
30. J. A. Demetrion, *J. Chromatog.*, 1968, **34**, 342.
31. S. F. Contractor and P. Jomain, *Clin. Chim. Acta*, 1966, **14**, 535.
32. M. G. M. Balemans, I. Ebels and D. M. A. Vonk-Visser, *J. Neurovisc. Rel.*, 1970, **32**, 65. (See also I. Ebels and M. G. M. Balemans, *ibid.*, in the press).
33. N. J. Giarman, D. X. Freedman and L. Ricard-Ami, *Nature*, 1960, **186**, 480.
34. Ch. Owman, *Int. J. Neuropharmacol.*, 1964, **2**, 105.
35. C. J. W. Brooks and E. C. Horning, *Anal. Chem.*, 1964, **36**, 1540.
36. H. M. Fales and J. J. Pisano, *Anal. Biochem.*, 1962, **3**, 337.
37. E. R. Cole and G. Crank, *J. Chromatog.*, 1971, **61**, 225.
38. E. R. Cole, G. Crank and J. Rowe, unpublished results.
39. D. T. N. Polley and R. Melidi, *J. Chromatog.*, 1968, **32**, 592.
40. K. H. Berry, H. E. Sutton, L. Cain and J. S. Berry, *Univ. Texas Publ.* No. 5109, 1951, **8**, 22.
41. M. D. Armstrong, K. F. N. Shaw, M. J. Gortatowski and H. Singer, *J. Biol. Chem.*, 1958, **232**, 17.
42. J. Harley-Mason and A. A. G. P. Archer, *Biochem. J.*, 1958, **69**, 60P.
43. O. Gerngross, K. Voss and T. Herfelt, *Ber.* 1933, **66**, 435.
44. S. Udenfriend and J. R. Cooper, *J. Biol. Chem.*, 1952, **196**, 227.
45. S. Udenfriend, H. Weissbach and C. T. Clark, *ibid.*, 1955, **215**, 337.
46. O. O. Mustala, *Ann. Med. Exp. Biol. Fenniae Suppl.*, 1965, **43**(8); *Chem. Abstr.*, 1966, **64**, 11536.
47. W. M. McIsaac, B. T. Ho, V. Estevez and D. Powers, *J. Chromatog.*, 1967, **31**, 446.
48. J. B. Jepson in I. Smith ed. *Chromatographic and Electrophoretic Techniques*, Vol. I, p. 196. Heinemann, London, 1960.
49. D. F. Bogdanski, A. Pletscher, B. B. Brodie and S. Udenfriend, *J. Pharmac. Exp. Therap.*, 1956, **117**, 82.
50. S. V. Konev, *Fluorescence and Phosphorescence of Proteins and Nucleic Acids*, p. 9. Plenum Press, New York, 1967.
51. M. G. M. Balemans and F. C. G. van de Veerdonk, *Experientia*, 1967, **23**, 906.
52. W. B. Quay, *Anal. Biochem.*, 1963, **5**, 51.
53. C. Dreux and D. Halter, *Clin. Chim. Acta*, 1970, **30**, 519.
54. R. P. Maickel and F. P. Miller, *Anal. Chem.*, 1966, **38**, 1937.

55. J. Korf and J. B. Sebens, *Clin. Chim. Acta*, 1970, **27**, 149.
56. D. Ames, R. Fleming and R. Hakanson, *J. Chromatog.*, 1968, **33**, 480.
57. N. Narasimbachari and J. Plant, *ibid*, 1971, **57**, 433.
58. G. Curzon and J. Giltrow, *Nature*, 1954, **173**, 314.
59. O. Boris and W. C. Ralston, *Proc. Soc. Exp. Biol. Med.*, 1951, **77**, 807.
60. A. B. Lerner and R. M. Wright, in *Methods of Biochemical Analysis*, Vol. VIII, 1960, ed. D. Glick. Interscience Publishers, New York.
61. C. L. Ralph, L. Hedland and W. Murphy, *Comp. Biochem. Physiol.*, 1967, **22**, 591.
62. C. L. Ralph and H. J. Lynch, *Gen. Comp. Endocrinol.*, 1970, **15**, 334.
63. A. J. Kastin and A. V. Schally, *Experientia*, 1966, **22**, 389.
64. H. Wiener, *New York State J. Med.*, 1968, **68**, 912.
65. E. Thring, *Acta Endocrinol.*, 1952, **10**, 295.
66. P. L. Wright, *Anat. Rec.*, 1946, **96**, 44.
67. E. H. Frieder, J. H. Fishbein and F. L. Hisaw, *Arch. Biochem.*, 1948, **17**, 187.
68. K. A. Shizume, A. B. Lerner and T. B. Fitzpatrick, *Endocrinol.*, 1954, **54**, 554.
69. W. Mori and A. B. Lerner, *ibid.*, 1960, **67**, 443.
70. L. Hogben and D. Sloane, *Proc. Roy. Soc, London*, 1931 **B108**, 10.
71. W. B. Quay, *Gen. Comp. Endocrinol.*, 1968, **11**, 253.
72. H. Waring, *Color Change Mechanisms of Cold Blooded Vertebrates*, Academic Press, New York, 1963.

Talanta, 1972, Vol. 19, pp. 1599 to 1604. Pergamon Press. Printed in Northern Ireland

MÖSSBAUER INVESTIGATION OF IRON-ALUMINIUM MIXED OXIDES

L. KORECZ, I. KURUCZ, G. MENCZEL, E. PAPP-MOLNÁR,
E. PUNGOR and K. BURGER
Department of Atomic Physics, Department of Experimental Physics and Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, and Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.

(*Received* 23 *February* 1972. *Accepted* 23 *March* 1972)

Summary—Mixed hydroxides of iron and aluminium have been precipitated from solutions containing iron and aluminium salts. The ratio of iron and aluminium was changed from 1:1 to 1:9. The mixed oxides produced by heating the hydroxides have been investigated by the Mössbauer effect. The Mössbauer spectra were composed of two systems of lines: one is due to magnetic splitting produced by α-Fe_2O_3, the other is due to quadrupole splitting (0·45 mm/s) which can be assigned to iron atoms in the lattice of α-Al_2O_3. The role of the anion of the solvated salts has also been investigated.

THE MÖSSBAUER isomer-shift is proportional to the change of electron density at the resonant nucleus. From the magnitude of the quadrupole splitting conclusions may be drawn regarding the symmetry of the surroundings (the electron shell) of the nucleus. Accordingly, changes in the chemical environment will change these parameters. The Mössbauer effect can be used to elucidate incorporation processes and to determine the proportion of Mössbauer atoms in different surroundings.

Metal hydroxides were precipitated from solutions containing different concentrations of iron(III) and aluminium(III) chlorides. The concentration ratio of iron to aluminium in the solution was varied from 1:1 to 1:9. The stock solution concentration was 0·1*M* for both aluminium and iron and the precipitation was carried out with 50% sodium hydroxide solution. The precipitates were dried and ignited at 1100° for 8 hr to give aluminium and iron oxides (M_2O_3). The aim of the present work was the examination of these mixed oxides.

The Mössbauer spectrum of hematite (α-Fe_2O_3) and of iron incorporated in corundum (α-Al_2O_3) has been examined many times.[1-7] These investigations were concerned with the magnetic behaviour of α-Fe_2O_3 and the phenomena of magnetic relaxation. Compounds of the composition $Al_{2-x}Fe_xO_3$ corresponding to the concentration range studied by us, have also been investigated. Dayal and co-workers[8] have prepared samples in a similar way and other authors have prepared compounds of this type by fusing Al_2O_3 with Fe_2O_3.[9]

EXPERIMENTAL

The investigations were carried out with a spectrograph (applying modulation with constant acceleration) constructed in the Department of Atomic Physics at the Eötvös University. The source was a stainless steel plate containing ^{57}Co (Radiochemical Centre, Amersham, England).

Samples were prepared from the substances to be investigated by pressing them between two thin aluminium foils into an even layer containing 30 mg/cm^2.

The measurements were carried out as described previously[10] with both source and sample at ambient temperature. The more important samples were also studied at liquid-nitrogen temperatures.

RESULTS AND DISCUSSION

The Mössbauer spectra obtained are complex and can be resolved into two superimposed line systems. One contains six magnetically split lines which can be shown to be due to α-Fe_2O_3. The other contains a quadrupole-split line with a splitting of 0·45 mm/s and a 0·27 mm/s isomer shift (compared to iron). These figures characterize an iron(III) atom bound by a relatively covalent bond. On the basis of data published by Bhide and co-workers[7] it can be assumed that this line is due to the iron incorporated into the corundum lattice.

Whereas at a 1:1 ratio of iron to aluminium the magnetically split spectrum is predominant at a 1:2 ratio, the appearance of an intense central quadrupole-split line indicates the changed environment of part of the iron. The intensity of the magnetically split lines (characteristic of α-Fe_2O_3) decreased with increase in the ratio of aluminium to iron, while the relative intensity of the quadrupole-split line increased. At iron to aluminium ratios of 1:7 and 1:8 only the central quadrupole-split line is obtained (Figs. 1 and 2). On separation of the two line systems the changes in the areas under the Mössbauer lines clearly show the variation in the ratio of the two different kinds of iron (Table I).*

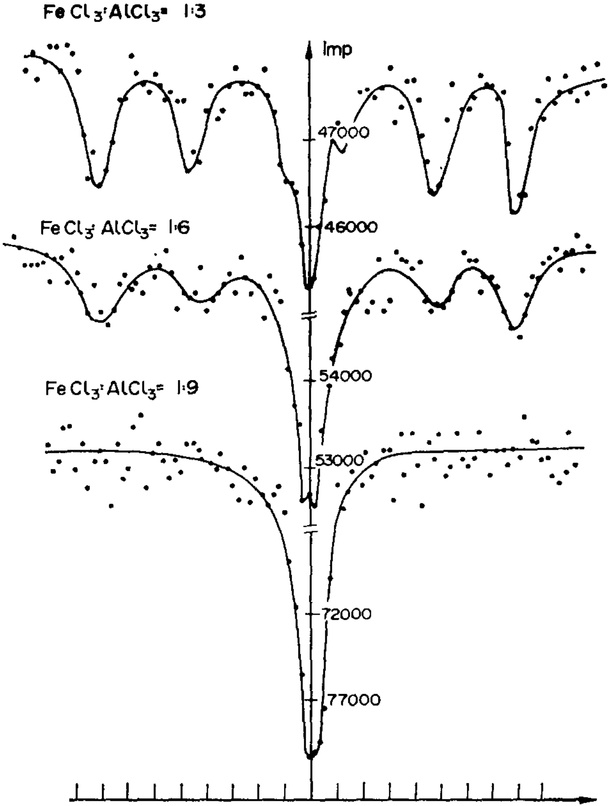


FIG. 1.—Mössbauer spectra of mixed oxides containing iron and aluminium in the ratios 1:3, 1:6 and 1:9.

* The probability of the Mössbauer effect, calculated on the basis of the areas under the absorption lines, for the magnetic line system (Fe:Al = 1:1) is $f = 0{\cdot}34 \pm 0{\cdot}05$, while for the central quadrupole-split line (Fe:Al = 1:9) it is $f = 0{\cdot}47 \pm 0{\cdot}05$.

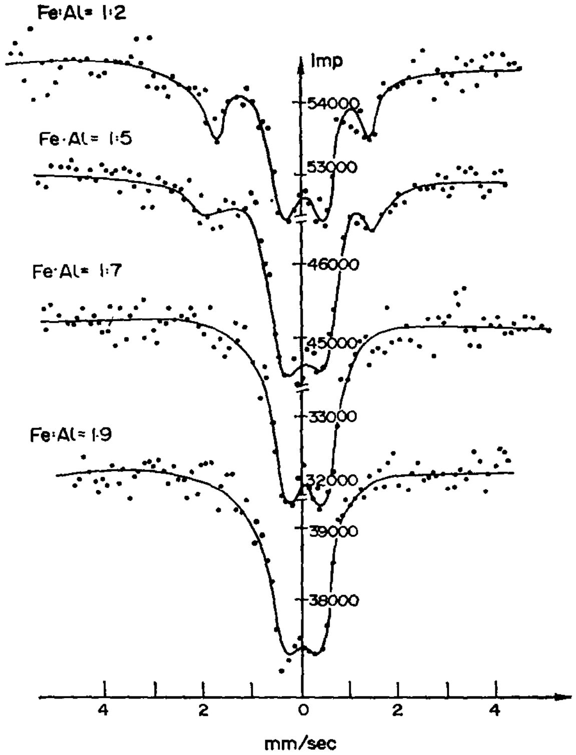


FIG. 2.—Central portions of the spectra of mixed oxides at higher resolution. The samples contained iron and aluminium in the ratios 1:2, 1:5, 1:7, and 1:9.

TABLE I.—AREAS OF MAGNETICALLY AND QUADRUPOLE-SPLIT LINES IN THE MÖSSBAUER SPECTRA OF SAMPLES HAVING VARYING INITIAL IRON AND ALUMINIUM CONCENTRATIONS

Fe:Al	Total area (normalized)	Area of the magnetically split line (normalized)	Area of the quadrupole-split line (normalized)
1:1	0·49	0·49	0
1:2	0·45	0·34	0·11
1:3	0·37	0·25	0·12
1:4	0·33	0·18	0·15
1:5	0·31	0·13	0·18
1:6	0·30	0·13	0·17
1:7	0·18	0·05	0·13
1:8	0·13	0·00	0·13
1:9	0·11	0·00	0·11

For those samples in which iron chloride and aluminium chloride were the starting materials, the area under the quadrupole-split line reached a maximum at a 1:5 iron:aluminium ratio, and decreased at lower Fe:Al ratios. At this maximum about 15–20% of the aluminium atoms are replaced by iron in the corundum lattice. At higher aluminium concentrations the decrease can be explained by the decrease of the total iron content of the sample.

The experimental results show that the relative amount of α-Fe_2O_3 diminishes with decreasing iron concentration and at the 1:9 iron:aluminium ratio only the mixed oxide is formed. Only a few aluminium atoms are incorporated into the iron oxide lattice since the magnetically split spectrum does not show significant changes, although this would appear possible from the similar size of the ionic radii (aluminium 0·05 nm, iron 0·06 nm).

The interpretation of our experimental results is supported by X-ray measurements. Some of our roentgenograms (Fig. 3) show that the samples consist of two components α-Fe_2O_3 and α-Al_2O_3. The intensity of the two line systems changes with increasing aluminium content, that due to corundum increasing and that due to hematite decreasing. At a 1:9 ratio only the lines characteristic of corundum can be detected. The increase in the lattice parameters for this sample compared with those of pure corundum indicates the incorporation of iron. The position of the iron oxide lines reveals a minute decrease in the lattice constant which may be due to the incorporation of aluminium ions.

Relaxation effects may also cause spectra[4] similar to the Mössbauer spectra obtained by us. However, our X-ray investigations and the fact that our Mössbauer

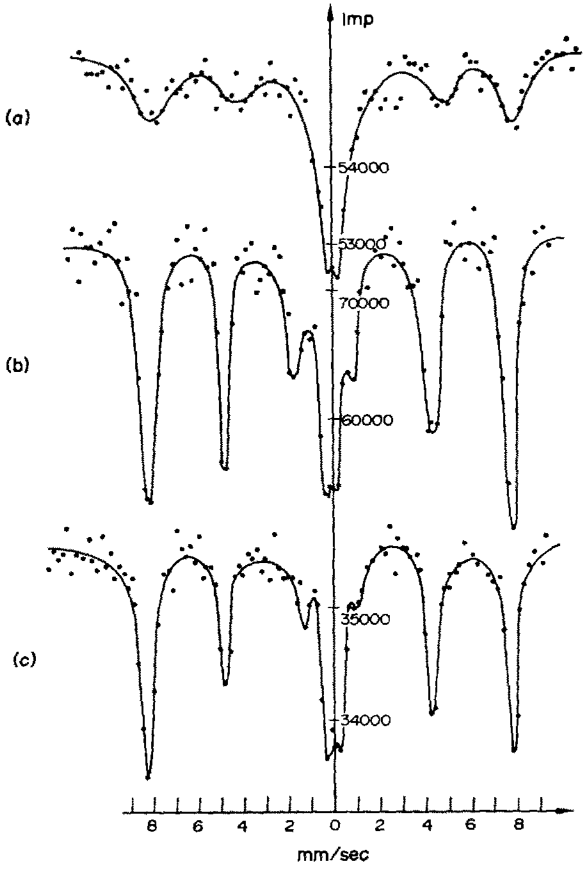


FIG. 4.—Mössbauer spectra of mixed oxides of iron and aluminium: (*a*) precipitated and ignited together (*b*) precipitated and ignited separately, then after mixing ignited once more (*c*) precipitated separately and ignited together. The initial Fe:Al ratio was 1:6.

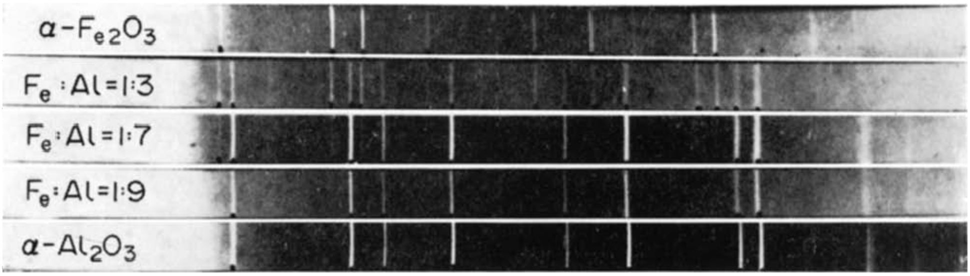


FIG. 3.—X-ray photographs of mixed oxides containing iron and aluminium in the ratios 1:3, 1:7 and 1:9 and of pure α-Fe_2O_3 and α-Al_2O_3.

spectra obtained at the temperature of liquid nitrogen were basically the same as the spectra recorded at room temperature, eliminate this possibility.

In order to decide whether the iron was incorporated during precipitation or upon ignition, measurements were made on samples where the possibility of incorporation in solution was excluded. The iron and aluminium hydroxides were precipitated and ignited separately and mixed in the form of their oxides. This mixture yielded only the Mössbauer spectrum of α-Fe_2O_3. Upon ignition the Mössbauer spectrum showed some incorporation effects (Fig. 4b) but less than that shown by samples prepared by co-precipitation. In some experiments the hydroxides were precipitated separately, dried at 130° and ignited together (Fig. 4c). In these samples the ratio of iron to aluminium was also 1:6 and a quadrupole-split line appeared in the Mössbauer spectrum. The intensity was the same as that in Fig. 4b, but smaller than that obtained with the sample prepared by co-precipitation (Fig. 4a).

Comparison of the area under the quadrupole-split lines with the total area shows a smaller incorporation effect in the case of a 6:1 aluminium:iron ratio, if the iron and aluminium samples are precipitated separately, than with a 2:1 aluminium:iron ratio if the samples are precipitated and ignited together. Accordingly, the incorporation must take place in the solution. Any incorporation during ignition has not been investigated in detail.

Experiments were carried out to study the effect of the nature of the anion upon the incorporation process. Samples were precipitated in the presence of sulphate and perchlorate ions. The behaviour of samples precipitated from solutions containing

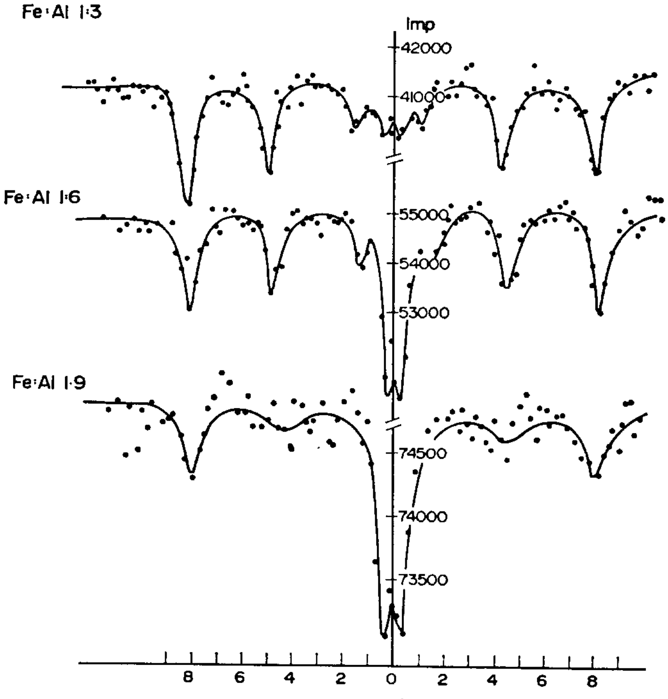


FIG. 5.—Mössbauer spectra of samples precipitated from sulphate solutions containing iron and aluminium in the ratios 1:3, 1:6 and 1:9.

chloride and perchlorate ions was similar, but those from solutions containing sulphate showed a smaller incorporation of iron. The magnetically split spectrum disappears at a greater aluminium:iron ratio and the increase of the central quadrupole doublet is slower. With iron and aluminium in a 1:3 ratio the quadrupole-split line is more intense for samples precipitated from chloride solution than for those from sulphate solution with a 1:6 iron:aluminium ratio. This phenomenon may be explained by assuming that the anions are co-ordinated to the iron and aluminium in the solution and that the strength of the metal–ligand bond influences the formation of the oxygen bridge in the hydroxides. It has been shown that sulphate ions are co-ordinated to aluminium and iron more strongly than are chloride ions.

Our results are in good agreement with the data of the oscillometric equilibrium measurements carried out by Pungor and Zapp[11] in an examination of aluminium hydrolysis and the effect of the anion on the composition of the polymer formed.

Zusammenfassung—Aus Lösungen, die Eisen- und Aluminiumsalze enthielten, wurden gemischte Hydroxide von Eisen und Aluminium ausgefällt. Das Verhältnis von Eisen und Aluminium wurde von 1:1 bis 1:9 variiert. Die durch Erhitzen der Hydroxide hergestellten gemischten Oxide wurden mit Hilfe des Mößbauereffekts untersucht. Die Mößbauerspektren setzten sich aus zwei Liniensystemen zusammen: eines beruht auf der durch γ-Fe_2O_3 hervorgerufenen magnetischen Aufspaltung, das andere auf Quadrupolaufspaltung (0,45 mm/s), die Eisenatomen im α-Al_2O_3-Gitter zugeschrieben werden kann. Auch die Rolle des Anions der solvatisierten Salze wurde untersucht.

Résumé—On a précipité des hydroxydes mixtes de fer et d'aluminium de solutions contenant des sels de fer et d'aluminium. Le rapport du fer à l'aluminium a été changé de 1:1 à 1:9. Les oxydes mixtes produits par chauffage des hydroxydes ont été étudiés par effet Mössbauer. Les spectres de Mössbauer sont composés de deux systèmes de raies: l'un est dû au dédoublement magnétique produit par α-Fe_2O_3, l'autre est dû au dédoublement quadrupole (0,45 mm/s) qui peut être attribué aux atomes de fer dans le réseau de α-Al_2O_3. On a aussi étudié le rôle de l'anion des sels solvatés.

REFERENCES

1. A. H. Muir, K. I. Ando and H. M. Coogan, *Mössbauer Effect Data Index* 1958-1965, Interscience, New York, 1966.
2. F. van der Woude, *Phys. Status Solidi*, 1966, **17**, 417.
3. Y. Nakamura, *Phys. Letters*, 1964, **12**, 178.
4. W. Kundig, H. Bömmel, G. Constabaris and R. H. Lindquist, *Phys. Rev.*, 1966, **142**, 327.
5. G. Cinadar, P. S. Flanders and S. Stikmann, *ibid.*, 1967, **162**, 419.
6. G. Vertheim, *Effect Mössbauera*, p. 133. Izdat. Mir, Moscow, 1966.
7. V. G. Bhide and S. K. Date, *Phys. Rev.*, 1968, **172**, 345.
8. R. R. Dayal, J. A. Gard and F. P. Glasser, *Acta Cryst.*, 1965, **18**, 574.
9. M. Schieber, R. B. Frankel, N. A. Blum and S. Foner, *J. Appl. Phys.*, 1953, **A66**, 585.
10. K. Burger, L. Korecz, P. Mag, U. Belluco and L. Busetto, *Inorg. Chim. Acta*, 1971, **5**, 362.
11. E. Pungor and E. Zapp, *Z. Anal. Chem.*, 1963, **197**, 404.

Talanta, 1972. Vol. 19, pp. 1605 to 1610. Pergamon Press. Printed in Northern Ireland

COULOMETRIC TITRATION OF ACIDS IN ISOPROPANOL—I

A RAPID DIRECT METHOD FOR THE DETERMINATION OF CARBON IN STEEL

B. METTERS, B. G. COOKSEY and J. M. OTTAWAY
Department of Pure and Applied Chemistry, University of Strathclyde,
Cathedral Street, Glasgow. C.1

(*Received* 9 *February* 1972. *Accepted* 7 *May* 1972)

Summary—A new procedure is described for the direct coulometric titration of the carbon dioxide liberated in the high-temperature combustion of steel. The carbon dioxide is absorbed in isopropanol containing 3% of ethanolamine and titrated with 100% titration efficiency with a constant current of 50 mA and spectrophotometric detection of the end-point. The accuracy and precision of the method have been established by the analysis of a wide range of standard steel samples.

THE DETERMINATION of carbon in steel by the non-aqueous titration of the carbon dioxide resulting from the high-temperature combustion of the sample in a stream of pure oxygen is now a well-established analytical technique. The titration procedure suggested by Blom *et al.*[1,2] in which the carbon dioxide is absorbed in pyridine and titrated with a solution of sodium methoxide dissolved in a mixture of methanol and pyridine has been modified by several workers[3–7]. Grant *et al.*[3] replaced the pyridine with dimethylformamide and used potassium methoxide in a benzene/methanol mixture as titrant. Jones *et al.*[4,6] added small amounts of ethanolamine to the same absorbent to give more efficient absorption of carbon dioxide and used tetra-n-butylammonium hydroxide in benzene/methanol or toluene/methanol as titrant. More recently, Ottaway *et al.*[8] suggested the replacement of the non-aqueous titrant with an aqueous solution of potassium hydroxide. All of these procedures were rapid, applicable to a wide range of steels and of sufficiently high accuracy. End-points have been detected visually with Thymol Blue or thymolphthalein as indicator.

The method of Ottaway *et al.*[8] was developed as a result of a wider investigation[9] into the feasibility of determining small amounts of carbon dioxide by a direct coulometric titration procedure in non-aqueous media. Back-titration methods have been reported in which the carbon dioxide is absorbed in aqueous barium hydroxide and the solution back-titrated coulometrically but the direct titration of carbon dioxide with electrogenerated base had not been described previously. Whymark[9] found that 100% coulometric titration efficiency could not be attained in the solvents necessary for carbon dioxide absorption, without the addition of large amounts of water. These additions of water, however, reduced the efficiency of carbon dioxide absorption in all solvents investigated and hydrolysed dimethylformamide to formic acid which was also titrated. Contrary to these results, Boniface and Jenkins[10] have recently described a method using a solution of ethanolamine in dimethylformamide containing 4% of water, in which no hydrolysis was observed. This method, although accurate and precise, is not as rapid as earlier methods since it requires approximately 8 min for a single determination.

In this paper a solution to the problems encountered by Whymark is suggested and 100% coulometric titration efficiency in non-aqueous solvents has been achieved without the addition of water. Based on these results a method is described for the coulometric determination of carbon in steel, using a solution of ethanolamine in isopropanol as absorbent.

EXPERIMENTAL

Reagents

The purest available chemicals were used. Tetraethylammonium bromide was purified by recrystallization.

Absorbent solutions

Dissolve 105·0 g of recrystallized tetraethylammonium bromide in isopropanol and dilute to 1 litre (solution A).

Dilute 11·5 ml of distilled water together with 6·0 ml of 0·1% w/v methanolic solution of thymolphthalein and 50 ml of ethanolamine to 500 ml with pyridine (solution B).

Dilute 200 ml of solution A together with 30 ml of ethanolamine and 10 ml of 0·1% w/v thymolphthalein solution in isopropanol to 1 litre with isopropanol (solution C).

Dilute 20 ml of solution A together with the required amount of ethanolamine (0, 1·0, 1·5, 2·0, 2·5, 3·0, 5·0, or 10·0 ml) to 100 ml with isopropanol (solution D).

Procedures

Recrystallization of tetraethylammonium bromide. Dissolve the crude tetraethylammonium bromide in the minimum amount of hot isopropanol. Cool slightly, then add acetone to precipitate the solid. Filter off, using a sintered-glass funnel, wash with acetone and dry immediately in an oven at 70°. Store in a desiccator to prevent absorption of water.

Measurement of absorption efficiency. A standard steel sample was combusted at 1250° in a stream of pure oxygen with pure tin as flux. Sulphur and nitrogen compounds were removed from the gas stream with manganese dioxide and magnesium perchlorate. The gas stream was passed though 50 ml of solution D and subsequently into 50 ml of previously neutralized pyridine solution B contained in a cylindrical absorption cell. The cell was fitted with a stopper through which the tip of a 10-ml burette was inserted. The pyridine solution was titrated with 0·05*M* potassium hydroxide and the amount of carbon dioxide not absorbed in the isopropanol solution was calculated.[8]

Determination of carbon in steel. The apparatus is outlined in Fig. 1. The constant-current generator has been described in detail by McMillan[11] and is similar to the valve circuit described by Glass and Moore.[12] This circuit gives currents of 50 mA at an output voltage of up to 200 V, which is necessary to avoid changes in the current during electrolysis in a purely non-aqueous medium. Before combustion of each steel sample the apparatus was flushed out with oxygen at 400 ml/min for 1 min. The absorption solution contained in the titration vessel, Fig. 2, was then titrated coulometrically to the end-point which was indicated by a suitable absorbance reading on an EEL spectrotitrator. The accurately weighed steel sample contained in a combustion boat with tin flux was pushed into the hot zone of the furnace. After 4 min the oxygen flow was switched off, the current (50 mA) was switched on simultaneously with a timing mechanism and the absorption solution retitrated to the marked end-point. During the titration the current was measured accurately with a standard resistance and a three-dial Tinsley potentiometer. Following subtraction of a blank value for the combustion boat and tin flux,

$$\%\mathrm{C} = \frac{12{\cdot}011}{96{,}486} \times \frac{i \times t}{W \times 10}$$

where i = current (mA), t = time (sec), W = weight of sample (g).

RESULTS AND DISCUSSION

Choice of supporting electrolyte

The main problem in a coulometric titration procedure is one of maintaining 100% coulometric titration efficiency. Whymark[9] showed that this efficiency could not be achieved in certain organic media when lithium chloride was used as supporting electrolyte unless substantial amounts of water were added, which then caused hydrolysis or a reduction in efficiency of carbon dioxide absorption. A more fundamental

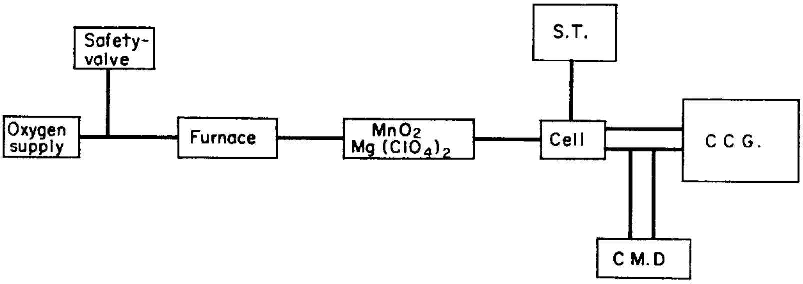


FIG. 1.—Apparatus for the coulometric determination of carbon in steel.
S.T. Spectrotitrator
C.C.G. Constant current generator
C.M.D. Current measuring device.

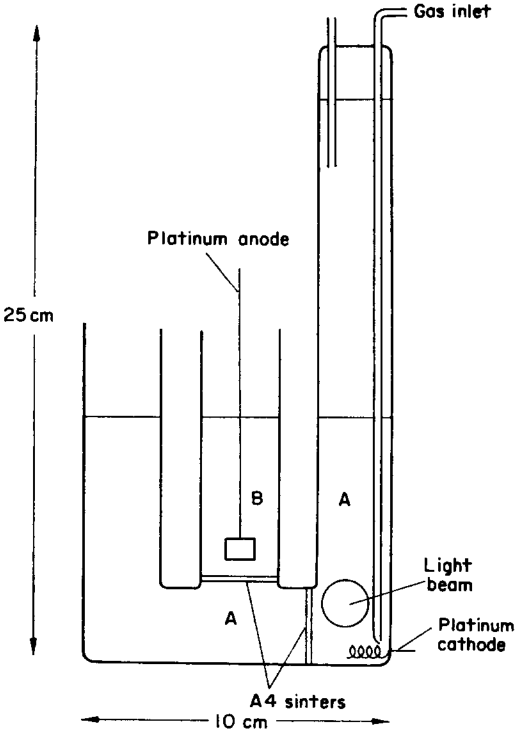


FIG. 2.—Titration cell.
A. Absorber solution
B. Methanol/tetraethylammonium bromide.

investigation into this problem[13] revealed that in isopropanol with lithium chloride as the supporting electrolyte, insoluble lithium hydroxide was formed on the electrode. The lithium hydroxide did not react with the acid being titrated and therefore the coulometric efficiency was reduced. When tetraethylammonium bromide was substituted as supporting electrolyte in the same solvent, no insoluble product formed on the cathode and 100% coulometric titration efficiency was obtained. When this same solution was electrolysed for several hours, and the products of electrolysis were precipitated with lithium bromide, analysis showed that the precipitate was lithium isopropoxide, suggesting that the solvent had been reduced to basic isopropoxide ions which in turn reacted completely with the acid being titrated.

Choice of ethanolamine concentration

The minimum amount of ethanolamine for efficient absorption of carbon dioxide was determined by passing the carbon dioxide through two absorption solutions. Any carbon dioxide not absorbed in the test solution was trapped in the second solution, which was known to absorb carbon dioxide efficiently, and then titrated manually (see procedure B). The results given in Table I show that only 3% of ethanolamine was necessary for quantitative absorption of carbon dioxide. The ethanolamine content was kept at a minimum since it was observed that the sharpness of the end-point decreased as the ethanolamine concentration increased, probably because of a buffer effect.

TABLE I.—EFFICIENCY OF CO_2 ABSORPTION IN ISOPROPANOL-ETHANOLAMINE SOLUTIONS

Ethanolamine, %	0	1·0	1·5	2·0	2·5	3·0	5·0	10·0
Absorption efficiency, %	20·0	88·0	93·0	96·5	99·0	99·9	99·9	99·9

Reaction sequence

The following reactions are thought to occur, and supporting evidence is described elsewhere.[13,14]

$$CO_2 + 2HO(CH_2)_2NH_2 \rightarrow (HO(CH_2)_2NHCOO)^-(HO(CH_2)_2NH_3)^+ \quad (1)$$

$$(C_2H_5)_4NBr \rightleftharpoons (C_2H_5)_4N^+Br^- \rightleftharpoons (C_2H_5)_4N^+ + Br^- \quad (2)$$

$$(CH_3)_2CHOH + e^- \rightarrow (CH_3)_2CHO^- + \tfrac{1}{2}H_2 \quad (3)$$

$$(CH_3)_2CH\,.\,O^- + (C_2H_5)_4N^+ \rightarrow (C_2H_5)_4N^+OCH(CH_3)_2^- \quad (4)$$

$$\begin{aligned}&(HO(CH_2)_2NHCOO)^-(HO(CH_2)_2NH_3)^+ + (C_2H_5)_4N^+OCH(CH_3)_2^- \\ &\rightarrow (HO(CH_2)_2NH_3)^+(OCH(CH_3)_2)^- + (C_2H_5)_4N^+\ HO(CH_2)_2NHCOO^- \quad (5)\end{aligned}$$

In reaction (1) carbon dioxide reacts with ethanolamine to form the ethanolamine salt of 2-hydroxyethylcarbamic acid.[14] In reaction (3), isopropanol is reduced with 100% coulometric efficiency to form basic isopropoxide ions[13] which are then available for the titration of the previously formed acid. It should also be mentioned that the reactions above do not necessarily predict the existence of free ions in isopropanol. In fact, it is probable that in reaction (2), for example, at equilibrium, ion-pairs predominate.

Carbon determinations

The determination of carbon in a wide range of steels was carried out by the procedure described above, and the results are given in Tables II and III. The method is accurate and fairly rapid, a single determination taking 5 min, of which 4 min are allowed for combustion of the sample with the apparatus available. The furnace available in our laboratory was unsuitable for the fast oxygen flow-rates necessary to

TABLE II.—DETERMINATION OF CARBON IN STEEL

Standard steel	Carbon content, % Certificate value	Carbon content, % Found	Sample weight g
MINCO*	0·062	0·062, 0·064, 0·060	1 (Pellet)
MINCO*	0·082	0·082, 0·084, 0·080, 0·080, 0·081, 0·083, 0·082	1 (Pellet)
Dalzell Std.† C.53	0·16	0·160, 0·166, 0·162, 0·156, 0·160	0·3
BS 219/3	0·31	0·31, 0·295, 0·30	0·2
BS 224/1	0·50	0·49, 0·49, 0·50	0·1
BS 403	0·72	0·75, 0·72, 0·72	0·1
BS 241/2	0·84	0·84, 0·82, 0·84	0·1
BS 401	1·06	1·054, 1·06, 1·054	0·1

* A sample from Mid-West Instrument Co. Inc., Belafield, Wisconsin, U.S.A.
† A sample from Dalzell Steel Works, Motherwell.

TABLE III.—REPRODUCIBILITY TEST ON B.S. 224/1, 0·50%C

% Carbon found, x_i
0·510
0·510
0·510
0·495
0·495
0·486
0·497
0·507
0·486
0·510

$\bar{x} = 0{\cdot}5006$

$\Sigma(x_i - \bar{x})^2 = 8{\cdot}96 \times 10^{-4}$

$$s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n - 1}}$$
$= 0{\cdot}010\%\text{C}$

Coefficient of variation = 2%

reduce the combustion time to under 2 min, which is the normal practice in the analogous volumetric procedures[4,6,8]. However, with such a furnace coupled to the present coulometric procedure, the time of determination may be reduced to between 2 and 3 min as the coulometric titration takes only 1 min to complete. The method therefore compares favourably in speed with the volumetric method which is commonly used in routine analysis for the control of the steelmaking process.

The main advantage of the method, as of any coulometric procedure, is that standardization is by direct reference to Faraday's law and no standardization of solutions or of the method itself is necessary. At least ten determinations are possible with each portion of absorbent solution. Although we have not attempted to do so, the method could easily be automated and could be made more rapid as described above and also by the use of higher generating currents. To our knowledge, only one other direct coulometric titration procedure has been reported for this determination[10] and this involves titration in a medium containing dimethylformamide with 3·5% of ethanolamine and 3·5% of water with potassium iodide as supporting electrolyte, a single determination taking about 8 min. Both coulometric methods obviously possess advantages from the point of view of automation and removal of the need for a separate titrant solution. The present method possesses a number of minor advantages in the use of a purely organic medium which would be expected to remove possible sources of error such as those due to hydrolysis of dimethylformamide,[9] or possible precipitation of inorganic compounds during titration. However, the main advantage of the present method would appear to be speed, which will possibly render it suitable for routine analysis and satisfactory as a replacement for the existing volumetric titration procedures.

Acknowledgement—We wish to thank W. Grierson and D. Mather of the Dalzell Steel Works, British Steel Corporation, Motherwell, for the gift of a tube furnace. We also wish to thank W. A. Alexander, our ex-colleague, who built the coulometer used in this work.

Zusammenfassung—Eine neue Arbeitsvorschrift für die direkte coulometrische Bestimmung des bei der Hochtemperaturverbrennung von Stahl freigesetzten Kohlendioxids wird angegeben. Das Kohlendioxid wird in Isopropanol absorbiert, das 3% Äthanolamin enthält, und mit 100-prozentiger Titrationsausbeute mit einem konstanten Strom von 50 mA und spektrophotometrischer Endpunktsanzeige titriert. Die Genauigkeit und Richtigkeit der Methode wurden durch Analyse einer großen Anzahl von Standard-Stahlproben ermittelt.

Résumé—On décrit une nouvelle technique pour le titrage coulométrique direct du gaz carbonique libéré dans la combustion à haute température de l'acier. Le gaz carbonique est absorbé dans de l'isopropanol contenant 3% d'éthanolamine et titré avec une efficacité de titrage de 100% avec un courant constant de 50 mA et une détection spectrophotométrque du point final. La précision et la fidélite de la méthode ont été établies par l'analyse d'une large gamme d'échantillons étalons d'aciers.

REFERENCES

1. L. Blom and L. Edelhausen, *Anal. Chim. Acta*, 1955, **13**, 120.
2. L. Blom, J. A. Stijntjes, J. A. van der Vliedervoet and J. A. Beeren, *Chim. Anal. (Paris)*, 1962, **44**, 302.
3. J. A. Grant, J. A. Hunter and W. M. S. Massie, *Analyst*, 1963, **88**, 134.
4. R. F. Jones, P. Gale, P. Hopkins and L. N. Powell, *ibid.*, 1965, **90**, 623.
5. A. Patchornic and Y. Shalitin, *Anal. Chem.*, 1961, **33**, 1887.
6. R. F. Jones, P. Gale, P. Hopkins and L. N. Powell, *Analyst*, 1966, **91**, 399.
7. P. Braid, J. A. Hunter, W. H. S. Massie, J. D. Nicholson and B. F. Pearce, *ibid.*, 1966, **91**, 439.
8. J. M. Ottaway, D. W. Whymark, B. Metters and B. G. Cooksey, *Talanta*, 1971, **18**, 773.
9. D. W. Whymark, *M.Sc. Thesis*, University of Strathclyde, 1969.
10. H. J. Boniface and R. H. Jenkins, *Analyst*, 1971, **96**, 37.
11. A. McMillan, *M.Sc. Thesis*, University of Strathclyde, 1965.
12. J. R. Glass and E. J. Moore, *Anal. Chem.*, 1960, **32**, 1265.
13. B. Metters, B. G. Cooksey, and J. M. Ottaway, *Talanta*, **19**, 1605.
14. J. M. Ottaway and D. W. Whymark, *Talanta*, 1972, **19**, 209.

Talanta, 1972, Vol. 19, pp. 1611 to 1622. Pergamon Press. Printed in Northern Ireland

BESTIMMUNG DES KOMPLEXTYPUS UND DER BESTÄNDIGKEITSKONSTANTE VON DISSOZIIERTEN KOMPLEXEN MIT HILFE TRANSFORMIERTER TITRATIONSKURVEN

J. Borák, Z. Slovák und J. Fischer
Forschungsinstitut für reine Chemikalien, Lachema, Brno, Tschechoslowakei

(*Eingegangen am* 5. *Januar* 1971. *Angenommen am* 23. *Mai* 1972)

Zusammenfassung—Die Methode der logarithmischen Transformation von photometrischen Titrationskurven zur Bestimmung der Komplexzusammensetzung wurde entwickelt und diskutiert. Sie eignet sich vor allem für eine sichere Unterscheidung von ein- und mehrkernigen Komplexen. Es wurde theoretisch abgeleitet und auf praktischen Beispielen gezeigt, daß die logarithmische Analyse zu eindeutigen Resultaten führt. Die Methode ist begrenzt durch zwei Bedingungen: (*a*) Bildung eines einzigen Komplexes in einem großen Konzentrationsgebiet; (*b*) es muß sich um relativ schwache Komplexe handeln.

In unseren früheren Mitteilungen beschäftigten wir uns mit einigen Gesetzmäßigkeiten, die vor allem bei der Bildung von schwachen Komplexen und bei Verwendung solcher Reaktionen bei den spektralphotometrischen Bestimmungen in Vordergrund treten.[1–4] Es wurden Beziehungen abgeleitet und in der Praxis benutzt,[1–3] die auf dem Massenwirkungsgesetz gegründet und für die Festlegung des Komplextypus und seiner Beständigkeitskonstante geeignet sind. Mit ähnlichen Transformationen beschäftigten sich bisher am meisten Newman[5,6] und Hume,[5–7] vor allem mit Rücksicht auf die Bestimmung von Beständigkeitskonstanten mit Hilfe spektralphotometrischer Messungen bei sukzessiver Bildung von einkernigen Komplexen. In seiner Arbeit, die dem Studium der Bildung von schwachen Komplexen eines Typus in der Lösung gewidmet ist, geht Klausen[8] von Werten aus, die mit Hilfe der Methode der kontinuierlichen Variationen (Job) erhalten werden. Die Methode wurde zur Unterscheidung von ein- und zweikernigen Komplexen angewandt und sie stützt sich auf eine Beziehung zwischen der Beständigkeitskonstante und den maximalen Extinktionswerten der Jobschen Kurven.

In dieser Arbeit wollen wir das Problem beurteilen, in wie weit man die Parameter der erhaltenen Funktion nach der logarithmischen Transformation einiger Titrationskurven für die eindeutige Festlegung des angenommenen Komplextypus und für die eindeutige Festlegung des angenommenen Komplextypus und für die Bestimmung seiner Beständigkeitskonstante eindeutig ausnutzen kann. Aus diesem Grund beschäftigten wir uns näher mit der Diskussion der allgemeinen Funktion bei den logarithmischen Analysen, und zwar besonders für die Fälle, bei welchen die stöchiometrischen Koeffizienten *a* und *b* des Komplexes M_aL_b nicht richtig vorausgesetzt wurden. Die Ergebnisse der allgemeinen Untersuchung führen dann zu Forderungen auf die experimentelle Ausführung der Titrationen. Die weiteren Erwägungen und Resultate gelten außer für die im Vordergrund stehenden photometrischen Titrationen auch für die weiteren "linearen Titrationskurven".[4]

Verwendete Symbole und Grundbeziehungen

A	Extinktion, gemessen gegen Blindansatz (Absorption des Kations vernachläßigbar)
A_0	Maximaler Wert von A. Allgemein wird A_0 bei genügend großem Titrantüberschuß direkt gemessen
K	Beständigkeitskonstante (scheinbare Konstante) nach Gl. (1)

$$K = \frac{[\mathrm{M}_a\mathrm{L}_b]}{(c_\mathrm{M} - a[\mathrm{M}_a\mathrm{L}_b])^a \cdot (c_\mathrm{L} - b[\mathrm{M}_a\mathrm{L}_b])^b} \tag{1}$$

$[\mathrm{M}_a\mathrm{L}_b]$	Gleichgewichtskonzentration des Komplexes $\mathrm{M}_a\mathrm{L}_b$, molar
a, b	Stöchiometrische Koeffizienten des gebildeten Komplexes
$c_\mathrm{L}, c_\mathrm{M}$	Totale Ligand- bzw. Metall-Konzentration, molar
k	Steigung der transformierten Titrationskurve im Punkt (ξ, η)
k_0	Steigung der transformierten Titrationskurve für $A \rightarrow 0$
k_{A_0}	Steigung der transformierten Titrationskurve für $A \rightarrow A_0$
α, β	Stöchiometrische Koeffizienten eines angenommenen Komplexes $\mathrm{M}_\alpha\mathrm{L}_\beta$; bei richtiger Voraussetzung gilt gleichzeitig $\alpha = a$ und $\beta = b$
Δ	Entfernung eines Punktes (ξ, η) der transformierten Titrationskurve von der Gerade der richtigen Transformation
Δ_0	Wert von Δ für $A \rightarrow 0$
Δ_{A_0}	Wert von Δ für $A \rightarrow A_0$
χ	Hilfskonstante

$$\chi = \frac{\varepsilon_{ab}^{a+b-1}}{K \cdot b^b}$$

ε_{ab}	Differentieller molarer Extinktionskoeffizient des Komplexes $\mathrm{M}_a\mathrm{L}_b$
ξ	Transformierte Titrationskurven—Abscissenachse
η	Transformierte Titrationskurven—Ordinatenachse

Logarithmische Transformation photometrischer Titrationskurven

Aus Gl. (1) folgt nach einfacher Umformung:[1,3]

$$-\log\left(b\frac{c_\mathrm{M}}{c_\mathrm{L}}A_0 - aA\right) = -\frac{1}{a}\log\frac{A}{(A_0 - A)^b} - \frac{1}{a}\log\frac{\varepsilon_{ab}^{a+b-1}}{K \cdot b^b} \tag{2}$$

In dieser Form gilt Gl. (2) für die Titration eines Ligandes L durch ein Kation M, d.h. für $A = A(c_\mathrm{M})_{c_\mathrm{L}=\mathrm{konst}}$. Für die Titration eines Kations durch ein Ligand, d.h. für $A = A(c_\mathrm{L})_{c_\mathrm{M}=\mathrm{konst}}$, gilt eine ganz analoge Beziehung, die man durch Austausch von M gegen L und a gegen b aus G. (2) erhalten kann. Die weiter abgeleiteten Beziehungen gelten deshalb nach dem Tausch der Symbole auch für die umgekehrten Titrationen. Für $a = 1$ ist die Beziehung (2) mit einer von Newman und Hume[5] abgeleiteten Gleichung praktisch identisch.

In der Praxis werden die gemessenen Titrationskurven nach Gl. (2) transformiert, indem man die Extinktionswerte A in das kartesische Koordinatensystem als Punkte (ξ, η) einträgt, wobei

$$\eta = -\log\left(\beta\frac{c_\mathrm{M}}{c_\mathrm{L}}A_0 - \alpha A\right) \text{ (Ordinatenachse)} \tag{3}$$

und

$$\xi = \log \frac{A}{(A_0 - A)^\beta} \text{ (Abscissenachse).} \tag{4}$$

Bei richtig gewählten α, β (d.h. $\alpha = a$ und gleichzeitig $\beta = b$) liegen die Punkte (ξ, η), die durch Transformation auch mehrerer Titrationskurven (bei verschiedenen Konzentrationen c_L) erhalten werden, an einer einzigen Gerade mit der geforderten Steigung $-1/a$. Dabei muß allerdings die Grundbedingung erfüllt werden, daß in der Lösung ein einziger genügend dissoziierter Komplex entsteht, und daß die gemessenen Extinktionswerte seiner Gleichgewichtskonzentration proportional sind. Auch die Kenntnis von A_0-Werten ist für die Transformation erforderlich.

Um die Eindeutigkeit und Richtigkeit dieser Aussage beurteilen zu können, ist es nötig den allgemeinen Verlauf der Beziehung (2) bei nicht richtig gewählten Koeffizienten α, β zu untersuchen.

In der Lösung entsteht in einem breiten Konzentrationsverhaltnis nur ein einziger Komplex

In diesem Fall sind die benötigten A_0-Werte durch die horizontalen Äste der Titrationskurven gegeben. Dabei gilt in guter Näherung: $[M_aL_b] = 1/b \cdot c_L$ und $A_0' : A_0'' : \ldots = c_L' : c_L'' : \ldots$, wobei A_0', A_0'' ... die Extinktionswerte an den horizontalen Ästen und c_L', c_L'' ... die entsprechenden totalen Ligandkonzentrationen bedeuten. Werden für die Transformation nach Gl. (3) und (4) die geschätzten Werte α, β benutzt, resultiert im Allgemeinen eine Kurve, und darüber hinaus sind die einzelnen transformierten Titrationskurven in Abhängigkeit von den verschiedenen c_L-Werten voneinander verschoben. Dieser Umstand ist für die richtige Beurteilung oft maßgebend, wie es bereits bei dem Studium der Komplexbildung von Arsenazo III mit Uranyl und Thorium empirisch gezeigt werden konnte.[3]

Den allgemeinen Verlauf der transformierten Titrationskurven kann man mathematisch optimal mit Hilfe einer Veränderlichen Δ untersuchen, die wir als die Entfernung der Punkte (ξ, η) von der hypothetischen Gerade definieren die bei richtig gewählten Werten $\alpha = a$ und $\beta = b$ gewonnen wäre.

Die Normalenform der Gl. (2) lautet:

$$\frac{a}{\sqrt{1 + a^2}} \log \left(\frac{c_M}{c_L} A_0 b - aA\right) + \frac{1}{\sqrt{1 + a^2}} \log \frac{(A_0 - A)^b}{A} - \frac{1}{\sqrt{1 + a^2}} \log \chi = 0 \tag{5}$$

Für die Entfernung Δ eines Punktes (ξ, η) von der Gerade (5) gilt:

$$\Delta = \frac{a}{\sqrt{1 + a^2}} \log \left(\frac{c_M}{c_L} A_0 \beta - \alpha A\right) + \frac{1}{\sqrt{1 + a^2}} \log \frac{(A_0 - A)^b}{A} - \frac{1}{\sqrt{1 + a^2}} \log \chi \tag{6}$$

Aus Gl. (2) berechnet man

$$\frac{c_M}{c_L} = \frac{1}{bA_0} \left[\frac{a\chi}{(A_0 - A)^b}\right]^{1/a} + \frac{a}{bA_0} A \tag{7}$$

Nach Einsetzen in (6) und Umformung resultiert für den gesuchten Wert von Δ:

$$\Delta = \frac{1}{\sqrt{1 + a^2}} \log \frac{(A_0 - A)^\beta}{a\chi} \left[\frac{\beta}{b} A^{1/a} \cdot \chi^{1/a} \cdot (A_0 - A)^{-b/a} + \frac{\beta}{b} aA - \alpha A\right]^a \tag{8}$$

Nach dieser Gleichung kann man die Entfernungen Δ der Punkte (ξ, η), die bei der Transformation bei falsch gewählten α, β gewonnen werden, von der Gerade der richtigen Transformation ($\alpha = a$ und $\beta = b$) berechnen.

Um einen anschaulicheren Überblick über den Verlauf der Funktion Δ zu bekommen, untersuchen wir erstens ihre Werte für die beiden extreme Zustände, d.h. den Anfang der Titration ($A \rightarrow 0$) und das Ende der Titration bei sehr großen Titrantüberschüssen ($A \rightarrow A_0$).

Für den Anfang der Titration ($A \rightarrow 0$) gilt:

$$\Delta_0 \equiv \lim_{A \to 0} \Delta = \frac{1}{\sqrt{2}} \log \left(\frac{\beta}{b} A_0^{-b} + \frac{\beta}{b\chi} - \frac{\alpha}{\chi} \right) A_0^{\beta} \tag{9}$$

für $a = 1$, und

$$\Delta_0 \equiv \lim_{A \to 0} \Delta = \frac{a}{\sqrt{1 + a^2}} \log \frac{\beta}{b} A_0^{(\beta - b)/a} \tag{10}$$

für $a > 1$.

Für das Ende der Titration ($A \rightarrow A_0$) gilt:

$$\Delta_{A_0} \equiv \lim_{A \to A_0} \Delta = 0 \tag{11}$$

für $\beta = b$,

$$\Delta_{A_0} \equiv \lim_{A \to A_0} \Delta = +\infty \tag{12}$$

für $\beta < b$, und

$$\Delta_{A_0} = \lim_{A \to A_0} \Delta = -\infty \tag{13}$$

für $\beta > b$.

Bei der Transformation von n Titrationskurven (n verschiedene c_L-Werte) resultiert in den Koordinaten ξ, η bei $a, b \neq \alpha, \beta$, die gleiche Anzahl von Kurven analoger Form. Die Verschiebung dieser transformierten Kurven voneinander folgt aus der allgemeinen Beziehung (8) für Δ, anschaulicher wird sie jedoch in einigen Fällen aus den Δ_0-Werten, die nach Gl. (9) und (10) berechnet werden. So z.B. folgt aus Gl. (10) bei $a > 1$ für zwei Werte A_0' und A_0'':

$$\begin{aligned} \Delta_0' - \Delta_0'' &= \frac{a}{\sqrt{1 + a^2}} \log \frac{\beta}{b} A_0'^{(\beta - b)/a} - \frac{a}{\sqrt{1 + a^2}} \log \frac{\beta}{b} A_0''^{(\beta - b)/a} \\ &= \frac{\beta - b}{\sqrt{1 + a^2}} \log \frac{A_0'}{A_0''} = \frac{\beta - b}{\sqrt{1 + a^2}} \log \frac{c_L'}{c_L''} . \end{aligned} \tag{14}$$

Falls $a = b = 2$ und $\alpha = \beta = 1$, wird die Entfernung von zwei transformierten Anfängen der Titrationskurven bei c_L' und c_L'' durch Gl. (15) gegeben:

$$\Delta_0' - \Delta_0'' = -\frac{1}{\sqrt{5}} \log \frac{c_L'}{c_L''} \tag{15}$$

Analog kann man aus Gl. (9) die Entfernung von zwei transformierten Anfängen der Titrationskurven für den Fall berechnen, in dem bei der Existenz eines Komplexes ML die Transformation irrtümlich für $\alpha, \beta = 2$ vorgenommen wurde:

$$\Delta_0' - \Delta_0'' = \frac{1}{\sqrt{2}} \log \frac{c_L'}{c_L''} \tag{16}$$

Nur in dem Fall, daß die stöchiometrischen Koeffizienten richtig vorausgesetzt wurden, bekommt man also bei der Transformation von mehreren Titrationskurven bei verschiedenen Ausgangskonzentrationen eine einzige resultierende Gerade mit der geforderten Steigung.

Neben den extremen Werten von Δ ist es für die Beschreibung der Funktion Δ sinnvoll, den Wert der Steigung ihrer Tangente in einem beliebigen Punkt zu berechnen. Falls man an der unter einer falschen Voraussetzung transformierten Titrationskurve einen pseudolinearen Abschnitt mit genügend von $-1/\alpha$ abweichender Steigung findet, wäre es dann für die Eliminierung der falschen Annahme ausreichend, nur eine einzige Titrationskurve zu transformieren.

Die Steigung der transformierten Titrationskurve in ihrem beliebigen Punkt (ξ, η)

$$k = \frac{\mathrm{d}\eta}{\mathrm{d}A} \Big/ \frac{\mathrm{d}\xi}{\mathrm{d}A} \tag{17}$$

kann man aus den Beziehungen (7), (3) und (4) berechnen. Nach der Ableitung resultiert für k:

$$k = \tag{18}$$
$$-\frac{(A - A_0)\left[a - \alpha\frac{b}{\beta} + \frac{1}{a}\chi^{1/a}A^{(1/a-1)}(A_0 - A)^{-b/a} + \frac{b}{a}\chi^{1/a}A^{1/a}(A_0 - A)^{(-b/a-1)}\right]}{(A_0 - A + \beta A)\left[a - \alpha\frac{b}{\beta} + (A_0 - A)^{-b/a}\chi^{1/a}A^{(1/a-1)}\right]}$$

Für die beiden oben diskutierten extremen Fälle ($A \rightarrow 0$, $A \rightarrow A_0$) gilt dann:

$$k_{A_0} \equiv \lim_{A \rightarrow A_0} k = -\frac{b}{a\beta} \tag{19}$$

$$k_0 \equiv \lim_{A \rightarrow 0} k = -\frac{1}{a} \tag{20}$$

Bei der Berechnung der Beziehungen (19) und (20) kann man entweder nach der l'Hopital'schen Regel, oder auch einfacher nach Multiplizieren des Zählers und des Nenners durch $(A_0 - A)^{b/a}$ [Gl. (19)] oder durch $A^{(1-1/a)}$ [Gl. (20)]. Aus Gl. (19) und (20) folgt, daß man mit Hilfe einer einzigen transformierten Titrationskurve die Existenz eines angenommenen Komplexes $M_\alpha L_\beta$ ausschließen kann, falls bei $A \rightarrow 0$, $\alpha \neq a$ und bei $A \rightarrow A_0$, $b/a\beta \neq 1/\alpha$.

Auf Grund der oben abgeleiteten Beziehungen kann man die Kurventypen darstellen, die bei der Transfromierung einer Titrationskurve unter nicht richtiger Annahme eines Komplexes $M_\alpha L_\beta$ bei der wirklichen Bildung eines Komplexes $M_a L_b$ resultieren. Diese Kurven sind in Abb. 1 und 2 für alle Kombinationen $a, b, \alpha, \beta = 1,2$ schematisch dargestellt. Die Grenzwerte Δ_0, Δ_{A_0}, k_0, k_{A_0} bzw. $\Delta_{\max}$ sind in Tab. I zusammengestellt (in den Klammern sind die Kurvenbezeichnungen aus Abb. 1 und 2 angeführt). Für alle diese Kurven gilt, daß $\mathrm{d}\xi/\mathrm{d}A > 0$ und $\mathrm{d}\eta/\mathrm{d}A < 0$, die einzelnen Punkte (ξ, η) liegen somit bei höheren A Werten an den Kurven rechts unten, bei sinkenden Extinktionen links oben. Die Grenzwerte k_{A_0} sind bei den einzelnen Kurven angegeben. Für alle Kurven in Abb. 1 gilt im Einklang mit Gl. (20) $k_0 = -1$, in Abb. 2 $k_0 = -0{,}5$.

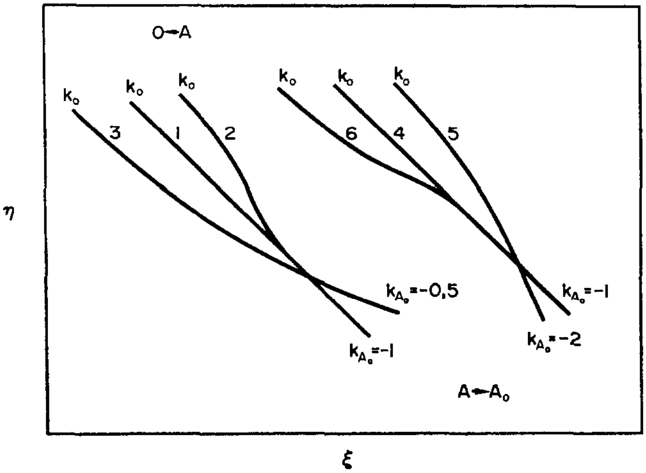


ABB. 1.—Typischer Verlauf transformierter Titrationskurven.
Kurven *1–3*—Es entsteht ein Komplex ML; Kurven *4–6*—Es entsteht ein Komplex ML_2
1—ML richtig vorausgesetzt; *2*—M_2L vorausgesetzt; *3*—M_2L_2 oder ML_2 vorausgesetzt;
4—ML_2 richtig vorausgesetzt; *5*—ML oder M_2L vorausgesetzt; *6*—M_2L_2 vorausgesetzt.

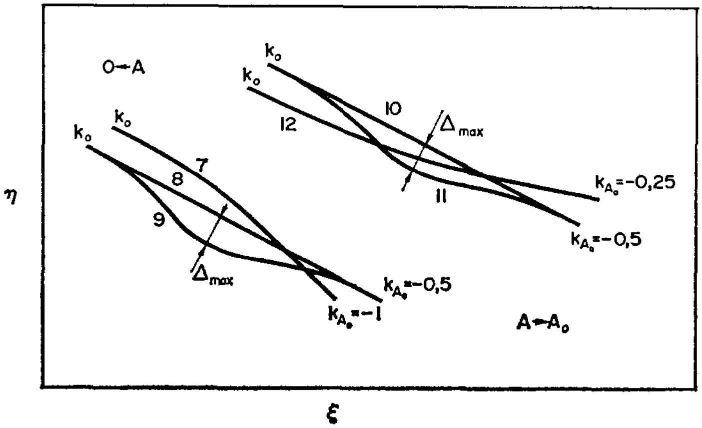


ABB. 2.—Typischer Verlauf transformierter Titrationskurven.
Kurven *7–9*—Es entsteht ein Komplex M_2L_2; Kurven *10–12*—Es entsteht ein Komplex M_2L *7*—ML oder M_2L vorausgesetzt; *8*—M_2L_2 richtig vorausgesetzt; *9*—ML_2 vorausgesetzt; *10*—M_2L richtig vorausgesetzt; *11*—ML vorausgesetzt; *12*—ML_2 oder M_2L_2 vorausgesetzt.

In Abb. 1 und 2 schneiden sich die Kurven *3*, *5*, *7* und *12* mit den Geraden der richtigen Transformation *1*, *4*, *8* und *10*. Ein Schnittpunkt entsteht nur dann, falls die Grenzwerte Δ_0 und Δ_{A_0} ein entgegengesetztes Vorzeichen haben. So z.B. für $\alpha = \beta = 2$ und $a = b = 1$ schneiden sich die Kurven nur, falls $A_0 > 0,5$ (bei $A = A_0 - 0,5$), wie es auch aus Gl. (8) für $\Delta = 0$ ersichtlich ist. Bei niedrigeren c_L-Konzentrationen ($A_0 < 0,5$) werden die transformierten Kurven in Richtung zu höheren ξ, η verschoben und sie bilden keinen Schnittpunkt mit der Gerade der richtigen Transformation.

TABELLE 1.—ENTFERNUNGEN DER PUNKTE (ξ, η) VON DEN GERADEN DER RICHTIGEN TRANSFORMATION UND STEIGUNGEN DER TRANSFORMIERTEN KURVEN IN GRENZGEBIETEN FÜR $A \to 0$ und $A \to A_0$

a,b \ α,β	$\alpha = \beta = 1$ (ML)	$\alpha = 1 \quad \beta = 2$ (ML_2)	$\alpha = 2 \quad \beta = 1$ (M_2L)	$\alpha = \beta = 2$ (M_2L_2)
$a = b = 1$ (ML)	(1) $\Delta = 0$ für $0 = A = A_0$ $k_0 = k = k_{A_0} = -1$	(3) $\Delta_{A_0} = -\infty$ $\Delta_0 = \frac{\sqrt{2}}{2} \log A_0\left(2 + \frac{A_0}{\chi}\right)$ $k_0 = -1 \quad k_{A_0} = -0{,}5$	(2) $\Delta_{A_0} = 0$ $\Delta_0 = \frac{\sqrt{2}}{2} \log\left(1 - \frac{A_0}{\chi}\right)$ $k_0 = -1 \quad k_{A_0} = -1$	(3) $\Delta_{A_0} = -\infty$ $\Delta_0 = \frac{\sqrt{2}}{2} \log 2A_0$ $k_0 = -1 \quad k_{A_0} = -0{,}5$
$a = 1$ $b = 2$ (ML_2)	(5) $\Delta_{A_0} = +\infty$ $\Delta_0 = \frac{\sqrt{2}}{2} \log \frac{1}{2}\left(\frac{1}{A_0} - \frac{A_0}{\chi}\right)$ $k_0 = -1 \quad k_{A_0} = -2$	(4) $\Delta = 0$ für $0 \leq A \leq A_0$ $k_0 = k = k_{A_0} = -1$	(5) $\Delta_{A_0} = +\infty$ $\Delta_0 = \frac{\sqrt{2}}{2} \log\left(\frac{1}{2A_0} - \frac{3A_0}{2\chi}\right)$ $k_0 = -1 \quad k_{A_0} = -2$	(6) $\Delta_{A_0} = 0$ $\Delta_0 = \frac{\sqrt{2}}{2} \log\left(1 - \frac{A_0}{\chi}\right)$ $k_0 = -1 \quad k_{A_0} = -1$
$a = 2$ $b = 1$ (M_2L)	(11) $\Delta_{A_0} = 0$ $\Delta_0 = 0$; $\Delta_{\max}$ für $A = \frac{1}{2}A_0$ $k_0 = -0{,}5 \quad k_{A_0} = -0{,}5$	(12) $\Delta_{A_0} = -\infty$ $\Delta_0 = \frac{\sqrt{5}}{5} \log 4A_0$ $k_0 = -0{,}5 \quad k_{A_0} = -0{,}25$	(10) $\Delta = 0$ für $0 \leq A \leq A_0$ $k_0 = k = k_{A_0} = -0{,}5$	(12) $\Delta_{A_0} = -\infty$ $\Delta_0 = \frac{\sqrt{5}}{5} \log 4A_0$ $k_0 = -0{,}5 \quad k_{A_0} = -0{,}25$
$a = b = 2$ (M_2L_2)	(7) $\Delta_{A_0} = +\infty$ $\Delta_0 = \frac{\sqrt{5}}{5} \log \frac{1}{4A_0}$ $k_0 = -0{,}5 \quad k_{A_0} = -1$	(9) $\Delta_{A_0} = 0$ $\Delta_0 = 0$; $\Delta_{\max}$ für $A = \frac{1}{3}A_0$ $k_0 = -0{,}5 \quad k_{A_0} = -0{,}5$	(7) $\Delta_{A_0} = +\infty$ $\Delta_0 = \frac{\sqrt{5}}{5} \log \frac{1}{4A_0}$ $k_0 = -0{,}5 \quad k_{A_0} = -1$	(8) $\Delta = 0$ für $0 \leq A \leq A_0$ $k_0 = k = k_{A_0} = -0{,}5$

In einigen Fällen geht Δ durch ein Maximum bei $0 < A < A_0$ (vgl. Kurven *9*, *11*). Die Extinktionswerte A, bei denen $\Delta = \Delta_{\max}$, wurden nach Einsetzen von a, b, α, β in Gl. (8) und der Bestimmung des Extrems mit Hilfe der ersten Ableitung berechnet. Wie es aus Kurven *9* und *11* und aus den Angaben für Δ_0 und Δ_{A_0} in Tab. I folgt, werden die Anfangs- und Endteile der transformierten Titrationskurven bei verschiedenen c_L in diesem Fall voneinander nicht verschoben. In dem Gebiet $0 < A < A_0$ wird jedoch die Verschiebung der einzelnen unter falschen Annahme transformierten Titrationskurven sichtbar, worüber man sich nach Einsetzen der konkreten Werten a, b, α, β in Gl. (8) und nach Auswertung des allgemeinen Ausdruckes für die Differenz $(\Delta' - \Delta'')$ für A_0' und A_0'' überzeugen kann.

Möglichkeiten der Anwendung logarithmischer Transformationen bei der stufenweisen Bildung mehrerer Komplexe

In einigen Fällen der stufenweisen Bildung mehrerer Komplexe wird die Bedingung, daß in der untersuchten Lösung nur ein Komplex entsteht, bei geeigneten experimentellen Bedingungen in guter Näherung erfüllt, nämlich bei einem genügenden Überschuß einer der reagierenden Komponenten. Zur Transformation eignen sich dabei die Anfangsteile der Titrationskurven. Den Grenzwert A_0 muß man mit Hilfe des unabhängig bestimmten molaren Extinktionskoeffizienten bestimmen, vgl. z.B. ref. 1–3, 9–11. Die Anwendung der Methode der logarithmischen Transformationen setzt in diesem Fall voraus, daß es sich um genügend dissoziierte Komplexe handelt (Transformation des Anfangsteiles der Titrationskurve). Kaum geeignet ist diese Methode für das Studium eines Systems, in welchem mehr als zwei verschiedene Komplexe nacheinander entstehen.

Anwendungsbeispiele

Die Anwendbarkeit der Methode der logarithmischen Transformationen photometrischer Titrationskurven und die Gültigkeit oben abgeleiteter Beziehungen wurden in der Praxis beim Studium der Komplexbildung von Arsenazo III mit Uranylionen und Thorium(IV) bewiesen.[3] Im Falle der Uranylkomplexen wurde die Existenz von zwei verschiedenen ML Komplexen mit $K_{ML} = 3 \cdot 10^3 – 1 \cdot 10^5$ in Abhängigkeit von den Versuchsbedingungen (pH) entdeckt. Die Möglichkeit einer eventuellen Bildung von M_2L_2 Komplexen wurde ausgeschlossen. Thorium(IV) bildet bei geeigneten Bedingungen vorwiegend Komplexe M_2L, ML_2 und zwei verschiedene ML Komplexe. Es wurden überall die Beständigkeitskonstanten bestimmt.

In Abb. 3 sind die transformierten photometrischen Titrationskurven von Sulfonazo III durch Ba^{2+}-Ionen gezeichnet. Gerade *1* wurde bei richtiger Voraussetzung ($a = b = 1$) für drei verschiedene Ligandkonzentrationen erhalten. Kurven *2*, *3* und *4* resultierten nach Transformation derselben Titrationskurven bei der falschen Voraussetzung $\alpha = \beta = 2$. Die an der Gerade *1* gezeichneten Punkte wurden aus Kurven *2–4* mit Hilfe der Gl. (8) errechnet. Die logarithmische Transformation bewies in diesem Fall eindeutig die Bildung eines ML-Komplexes.

Svoboda und Chromý[12] benutzten erfolgreich die logarithmischen Transformationen bei der Untersuchung der Komplexbildung von Magnesium mit Xylidyl Blue II (Magon). Es wurde die Existenz eines einzigen ML_2-Komplexes mit einem K-Wert von $(6{,}1 \pm 0{,}3) \cdot 10^9$ bei den gegebenen Bedingungen bewiesen.

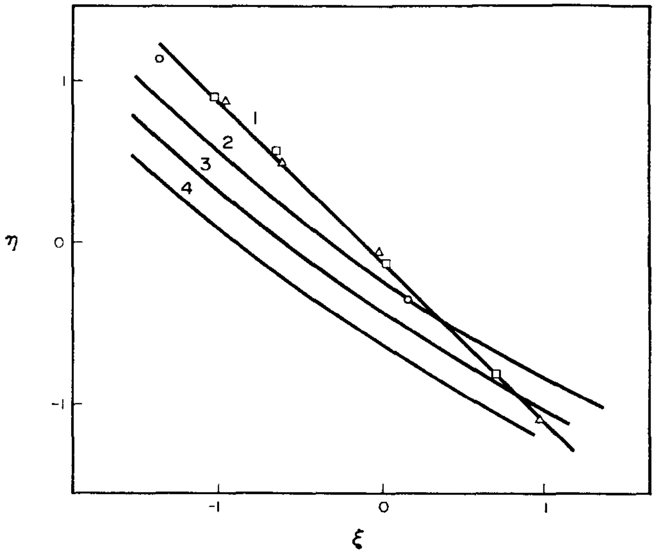


ABB. 3.—Logarithmische Transformation von drei photometrischen Titrationskurven von Sulfonazo III durch Bariumionen.

Kurven *2–4*—Transformation (ξ, η) für $\alpha = 2$, $\beta = 2$ (M_2L_2). *2*—$c_L = 2 \cdot 10^{-5}M$; *3*—$c_L = 5 \cdot 10^{-5}M$; *4*—$c_L = 1 \cdot 10^{-4}M$. Kurve *1*—richtige Transformation für $a = b = \alpha = \beta = 1$ (ML); die gezeichnete Kurve wurde von ref. 1, Abb. 8 übernommen, die markierten Punkte aus den falsch transformierten Kurven *2–4* als △ nach Gl. (8) berechnet (○ aus *2*; △ aus *3* und □ aus *4*).

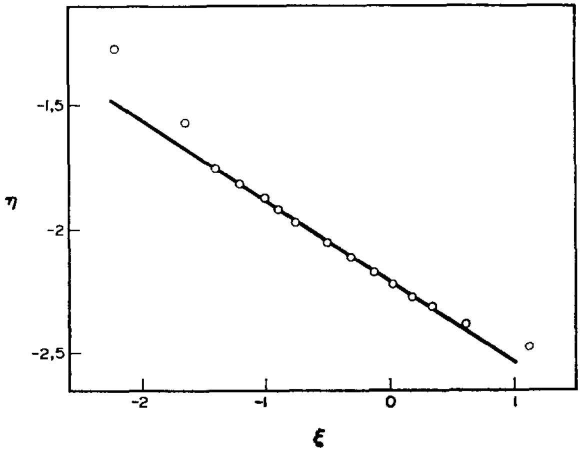


ABB. 4.—Logarithmische Transformation einer Titrationskurve von Azomethin durch Eisen(II).

Ein Komplex ML_3 richtig angenommen. Die experimentellen Angaben von Asmus[13] übernommen.

Asmus[13] widmete sich der Reaktion von Eisen(II) mit Azomethin (ein Kondensationsprodukt von Pyridin-2-aldehyd mit Sulfanilsäure) und stellte fest, daß ein einziger stark dissoziierter ML_3-Komplex gebildet wird. In der erwähnten Arbeit[13] (Seite 112) sind in einer Tabelle die gemessenen Werte der Extinktionen an einer Titrationskurve gegeben; wir haben uns erlaubt diese Titrationskurve logarithmisch zu transformieren. In Abb. 4 ist die resultierende transformierte Titrationskurve für

$\alpha = 1, \beta = 3$ gezeichnet. Die Steigung der Gerade beträgt $-0{,}326$ (daraus $b = 3{,}08$), der berechnete Wert von $1/K$ ist $4{,}26 \cdot 10^{-5}$ in ausgezeichneter Übereinstimmung mit der Angabe von Asmus $4{,}3 \cdot 10^{-5}$. Für die Transformation wurde $A_0 = 1{,}565$ aus dem angegebenen molaren Extinktionskoeffizienten ausgerechnet. In der Praxis könnte man in diesem Fall A_0 direkt bei einem genügenden c_L-Überschuß oder nach[1–3,9–11] bestimmen. Der gebildete Komplex ist stark dissoziiert, für die eindeutige Aussage genügt es, nur eine einzige ganze Titrationskurve zu transformieren. Die Abweichungen beider äußersten Teile der transformierten Titrationskurve von dem linearen Verlauf sind wahrscheinlich durch Meßfehler bei sehr kleinen Extinktionsmessungen, bzw. durch eine kleine Differenz in dem angenommenen Wert von A_0, bedingt.

SCHLUSSFOLGERUNGEN UND DISKUSSION

Es wurden allgemeine aus dem Massenwirkungsgesetz folgende Beziehungen abgeleitet, die eine eindeutige Interpretation der photometrischen Titrationskurven mit dem Ziel der Bestimmung der stöchiometrischen Koeffizienten des gebildeten Komplexes ermöglichen. Diese Beziehungen wurden an dem konkreten Beispiel aller Kombinationen a, b, α, $\beta = 1{,}2$ veranschaulicht. Auf ähnlicher Weise können analoge Gleichungen auch für andere Komplexe (z.B. 1:3) berechnet werden. Die Bildung vorwiegend eines einzigen Komplexes in einem weiten Konzentrationsgebiet wird vorausgesetzt.

Bei der richtigen Wahl des Komplextypus werden immer zwei Kriterien erfüllt.

1. Die transformierten Titrationskurven haben einen linearen Verlauf und den geforderten Wert der Steigung.
2. Die transformierten Punkte mehrerer bei verschiedenen Konzentrationen des zu titrierenden Stoffes erhaltenen Titrationskurven liegen an einer einzigen Gerade.

Falls die transformierte Titrationskurve keinen linearen Charakter aufweist, wird auch die zweite Forderung nicht erfüllt. In diesem Fall ist die Voraussetzung der stöchiometrischen Koeffizienten falsch, oder die Bedingung der überwiegenden Bildung eines einzigen Komplextypus blieb unerfüllt.

Aus den Achsenabschnitten kann man bei richtiger Transformation leicht den Wert von χ bestimmen, und daraus laut Definition die Stabilitätskonstante K berechnen:

$$\eta = -\frac{1}{a}\log\chi \qquad (\text{für } \xi = 0) \tag{21}$$

$$\xi = \log\chi \qquad (\text{für } \eta = 0) \tag{22}$$

Den dazu benötigten Wert des Extinktionskoeffizienten ε_{ab} erhält man mit Hilfe des Wertes A_0 aus der bekannten Grundbeziehung

$$A_0 = \frac{1}{b}\varepsilon_{ab}c_L \tag{23}$$

Aus Gl. (8) bzw. (21) und (22) folgt, daß bei den experimentellen Messungen der Titrationskurven alle Bedingungen äußerst konstant gehalten werden müssen, da auch eine relativ kleine Änderungen in K-Werten zwischen den einzelnen Versuchen (bedingt z.B. durch andere Ionenstärke, pH, Temperatur) eine Verschiebung der Geraden in Koordinaten ξ, η zur Folge hat. Wird also als Resultat der Transformation von mehreren Titrationskurven die Existenz von parallelen Geraden mit der geforderten

Steigung beobachtet, ist es wahrscheinlich, daß die Wahl des Komplextypus richtig war, die einzelnen Titrationskurven jedoch nicht bei vergleichbaren Bedingungen erhalten wurden.

Die beschriebene Methode eignet sich besonders für die Untersuchung bedeutend dissoziierter Komplexe [$K^{1/(a+b-1)} < 10^5$]. In diesem Fall ist es möglich den Typus und die Beständigkeitskonstante des gebildeten Komplexes durch die Transformation einer einzigen Titrationskurve zu bestimmen, da der starken Dissoziation wegen praktisch die ganze Kurve transformierbar ist und deshalb der lineare Verlauf der transformierter Kurve in einem großen Abschnitt nachweisbar ist.

Bei relativ festeren Komplexen ($K^{1/(a+b-1)} \sim 10^5$–10^6) kann man nur die gekrümmten Teile der Titrationskurven, oder sogar nur die einzelnen Punkte mehrerer Kurven bei $c_M/c_L = a/b$, wo der sich bildende Komplex am meisten dissoziiert, transformieren. Auch hier ist die Bedingung der alleinigen Bildung eines einzigen Komplexes wichtig (wegen der Bestimmung von A_0 aus den horizontalen Ästen der Titrationskurven). Bei festeren Komplexen steigern sich auch die Forderungen auf die Genauigkeit aller Extinktionsmessungen. Die Anwendung der Methode der logarithmischen Transformationen bietet sich auch für das Studium von festen Komplexen beim Ausnutzen von Konkurrenzreaktionen ein. Bei dieser Reaktion, die zur Erniedrigung des K-Wertes führt, dürfen jedoch keine ternäre Komplexe gebildet werden.

Soll die Methode der logarithmischen Transformation ihre Anwendung auch in Fällen finden, bei welchen die Bedingung der praktisch ausschließlichen Bildung eines einzigen Komplexes nur in einem begrenzten Gebiet der Werte von c_M/c_L (z.B. bei $c_L \gg c_M$) erfüllt wird, müssen immer mehrere Titrationskurven bei verschiedenen Konzentrationen des zu titrierenden Bestandteiles transformiert werden. Man beobachtet dann die Steigungen und die Verschiebung der erhaltenen transformierten Kurven. Werden die beiden oben formulierten Bedingungen gleichzeitig in einem bestimmten Konzentrationsgebiet erfüllt, bedeutet es, daß hier überwiegend der vorausgesetzte Komplex existiert.

Summary—A method is presented for the logarithmic transformation of photometric titration curves, with the aid of which it is possible to differentiate with certainty between mononuclear and polynuclear complexes. The mathematical expressions are derived, and applied to practical examples, leading to unequivocal conclusions. The method suffers from two limitations—over a wide range of concentrations only one complex should be formed, and it must be a relatively weak one.

Résumé—On présente une méthode pour la transformation logarithmique des courbes de titrage photométrique, à l'aide de laquelle il est possible de faire avec certitude la différence entre complexes mononucléaires et polynucléaires. On en déduit les expressions mathématiques et les applique à des exemples pratiques, menant à des conclusions sans équivoque. La méthode présente deux limitations: dans un large domaine de concentrations seulement un complexe doit être formé, et il doit être relativement faible.

LITERATURE

1. Z. Slovák, J. Fischer und J. Borák, *Talanta*, 1968, **15**, 831.
2. *Idem*, *ibid.*, 1969, **16**, 215.
3. J. Borák, Z. Slovák und J. Fischer, *ibid.*, 1970, **16**, 215.
4. J. Fischer, Z. Slovák und J. Borák, *ibid.*, 1971, **18**, 615.

5. L. Newman und D. Hume, *J. Am. Chem. Soc.*, 1957, **79**, 4571.
6. *Idem*, *ibid.*, 1957, **79**, 4576.
7. E. Burns und D. Hume, *ibid.*, 1957, **79**, 2704.
8. K. S. Klausen, *Anal. Chim. Acta*, 1969, **44**, 377.
9. E. Kwiatkowski, *Roczniki Chem.*, 1963, **37**, 481.
10. G. Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.
11. N. P. Komar, *Zh. Analit. Khim.*, 1950, **5**, 139.
12. V. Svoboda und V. Chromý, *Anal. Chim. Acta*, 1971, **54**, 121.
13. E. Asmus, *Z. Anal. Chem.*, 1960, **178**, 104.

Talanta, 1972, Vol. 19, pp. 1623 to 1632. Pergamon Press. Printed in Northern Ireland

STUDIES OF COPPER(II) SULPHIDE ION-SELECTIVE ELECTRODES

GILLIS JOHANSSON and KERSTIN EDSTRÖM
Department of Analytical Chemistry, University of Umeå, 901 87 Umeå, Sweden

(*Received* 1 *March* 1972. *Accepted* 7 *May* 1972)

Summary—Changes in liquid junction potentials in copper(II) solutions were measured when different reference electrodes were used. The slope and intercept of a calibration curve for a copper-selective electrode will depend on the selection of reference electrode. The condition of the electrode surface of an Orion copper-selective electrode was studied microscopically and the influence of redox potential on stability of the electrode against corrosion is discussed. Oxidizing solutions will produce pits at dislocations in the material and there will be a mixed electrode potential. The slope, stability, and speed of response are much lower when the surface contains pits. Diamond-polishing was shown to improve the electrode significantly.

IN RECENT years a number of papers on the behaviour of ion-selective electrodes have appeared in the literature. Most of these have given a simplified picture of the electrode behaviour and the manufacturers' literature has also tended to give an idealistic impression. When a need arose to test the ion radical electrodes described recently[1] and compare them with the sulphide electrodes, a more thorough investigation of the latter was necessary. This paper reports such an investigation of a copper(II) ion-electrode, namely the Orion copper sulphide electrode.[2]

An electrode is said to have a Nernstian or "theoretical" slope of the calibration curve if this equals $(RT \ln 10)/zF$, *i.e.*, 59·2 and 29·6 mV/decade at 25° for univalent and bivalent ions respectively. These values should be obtained only if a number of conditions are fulfilled. The most important prerequisites are that the variation in liquid-junction potential, the changes in activity coefficients and the changes in the activity of the reference ion in the solid electrode material are negligible. The activity of the reference ion in the surface layer of the electrode material is tactily assumed to be constant but usually no experiments have been made to test this assumption. Sato[3] has discussed the electrode behaviour for varying ion activity in the surface. Departures from the simple Nernst's law, due to cracks and pits in the surface, will be discussed in this paper.

EXPERIMENTAL

Electrodes

An Orion Cupric Ion Electrode 94-29 A and Orion Double Junction Reference Electrodes 90-02 were used. The bridge solution of the reference electrode was Orion 90-00-02 filling solution, 2*M*-potassium nitrate, 1*M* potassium nitrate, or 1*M* sodium nitrate. A Radiometer Calomel Electrode K 401 with saturated potassium chloride solution as bridge solution was also used.

Procedure

Potentiometric measurements were made in a Metrohm titration cell, EA 880-20. Solutions were prepared immediately before measurement, by dilution of a 0·1*M* stock solution. The dilution was made with an Oxford Sampler micropipete system. The cell was filled with 27 ml of solution and stirred with a magnetic follower. The measurements were then made at room temperature, 23°. Potential readings were made to the nearest 0·1 mV and in some cases to 0·01 mV. The electrodes were washed thoroughly with distilled water between the measurements. An electrode switch was used when several electrodes were studied simultaneously.

Surface studies

The electrode surface was studied with an inverted metal polarizing microscope, Zeiss UP 1, with a Polaroid camera attachment. The objectives were of the type Zeiss Epiplan, 4x, 8x, 16x, 40x, and 80x. The copper sulphide electrode was polished with a diamond paste of the smallest grain size, DP-paste type C (Struers, Copenhagen), in a polishing machine running at 125 rpm. A support held the electrode orthogonal to the turntable.

Calculations

For calculation of the liquid-junction potential the following constants were used: $\lambda^{\circ}_{Na^+} = 50{\cdot}1$, $\lambda_{K^+}{}^{\circ} = 73{\cdot}5$, $\lambda^{\circ}_{Cu^{2+}} = 53{\cdot}6$, $\lambda^{\circ}_{Cl^-} = 76{\cdot}35$, $\lambda^{\circ}_{NO_3^-} = 71{\cdot}46$ ohm^{-1}. cm^2. equiv.$^{-1}$. Figure 9 was constructed by using the following constants: $E^{\circ}_{Cu^{2+}/Cu} = 0.337$ V, $E^{\circ}_{Cu^{2+}/Cu^+} = 0{\cdot}153$ V, $E^{\circ}_{S^{2+}/S} = -0{\cdot}48$ V, $E^{\circ}_{Ag^+/Ag} = 0{\cdot}799$ V, and the solubility products: $K_{sp}(CuS) = 10^{-36.1}$ and $K_{sp}(Ag_2S) = 10^{-49{\cdot}4}$.

RESULTS AND DISCUSSION

Liquid-junction potentials

There are large differences in liquid-junction potentials between different bridge solutions used to connect the reference electrode to the sample solution. Figure 1 shows the difference in liquid-junction potentials between a reference electrode containing 2*M* potassium nitrate and other reference electrodes using different bridge solutions. The measurements were made in copper(II) nitrate solutions and in two salt solutions. Figure 2 shows the differences when the ionic strength was kept constant in the copper(II) nitrate solutions, $I = 0{\cdot}3$, by addition of potassium nitrate. It is seen that even when the ionic strength was kept constant there was a significant variation in the liquid-junction potential. This variation may cause a curved calibration graph which might be confused with deviations from Nernst's law. A calibration curve of an ideal ion-selective electrode will thus result in a curved calibration curve, the curvature being dependent on the selected reference electrode. If on the other hand a procedure is used in which the best straight line is drawn through the calibration points an analytical error of up to 20% may occur.

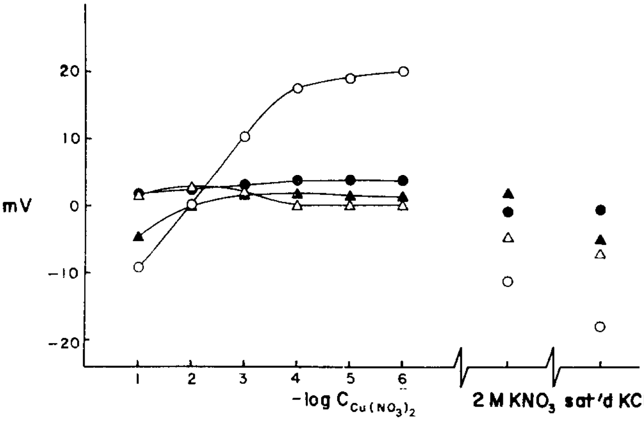


FIG. 1.—Difference in liquid-junction potential measured between a double-junction reference electrode containing 2*M* KNO_3 and a double-junction reference electrode containing
○ 1*M* $NaNO_3$
● Orion 90-00-02 filling solution
▲ 1*M* KNO_3
△ saturated KCl solution (Radiometer K 401)
immersed in solutions of $Cu(NO_3)_2$ with varying ionic strength and into two salt solutions.

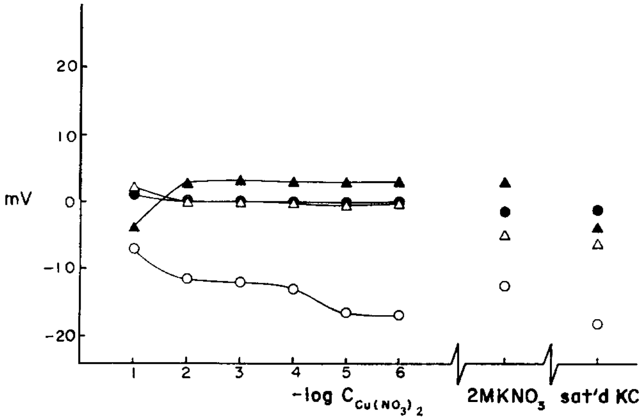


FIG. 2.—Difference in liquid-junction potential measured between a double-junction reference electrode containing $2M$ KNO_3 and a double-junction reference electrode containing
○ $1M$ $NaNO_3$
● Orion 90-00-02 filling solution
▲ $1M$ KNO_3
△ saturated KCl solution (Radiometer K 401)
immersed in solutions of $Cu(NO_3)_2$ with constant ionic strength, $I = 0{\cdot}3$, obtained by addition of KNO_3 and into two salt solutions. (100 mV was subtracted from all the readings with the $NaNO_3$ bridge solution.)

Figures 1 and 2 show only the difference between two liquid-junction potentials and it is not possible to measure the variation of a single liquid-junction potential independent of the determination of single ion activities. It is, however, possible to make approximate calculations of a single liquid-junction potential.

Henderson's equation gives the liquid-junction potentials for a "continuous mixture" junction

$$E_j = -\frac{RT}{F}\int_1^2 \sum \frac{T_i}{z_i}\,\mathrm{d}\ln c_i - \frac{RT}{F}\int_1^2 \sum \frac{T_i}{z_i}\,\mathrm{d}\ln \gamma_i = E_{jc} + E_{j\gamma}$$

where T_i is the transport number, z_i the charge, c_i the concentration and γ_i the activity coefficient. The first term, E_{jc}, can be evaluated if the transport number is assumed to be constant. The second term representing the non-ideal contributions cannot be evaluated directly. The first term was evaluated by using a computer programme. Figure 3 shows a plot of the differences in E_{jc} between a number of bridge solutions and $2M$ potassium nitrate, in copper(II) nitrate solutions and in two salt solutions. Figure 4 is a corresponding plot of a calculation made for copper(II) nitrate solutions in which the ionic strength was kept constant, $I = 0{\cdot}3$, by addition of potassium nitrate. If it had been possible to calculate correct liquid-junction potentials, Figs. 3 and 4 should have been identical to Figs. 1 and 2 respectively. As the agreement between calculated and measured differences was rather poor the calculation seems to be of limited value.

It is desirable to select a bridge solution which is likely to give a small variation in liquid-junction potential. The mobility of potassium ions is almost equal to the mobility of nitrate ions and therefore a salt bridge containing potassium nitrate

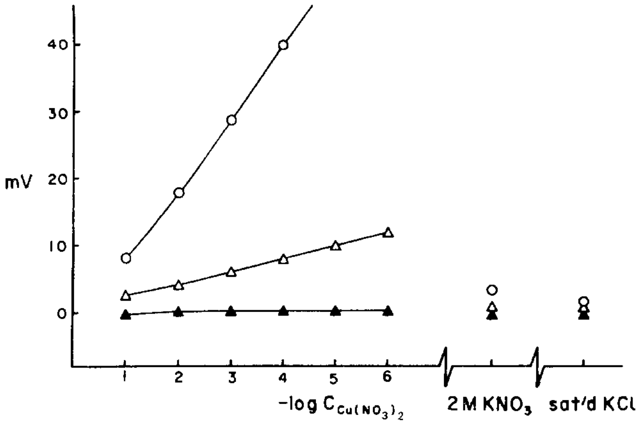


FIG. 3.—Calculated differences in liquid-junction potential between a bridge solution of $2M$ KNO_3 contacting copper and salt solutions and a bridge solution of

○ $1M$ $NaNO_3$
▲ $1M$ KNO_3
△ saturated KCl

contacting the same solutions. The ionic strengths of the copper solutions were varied.

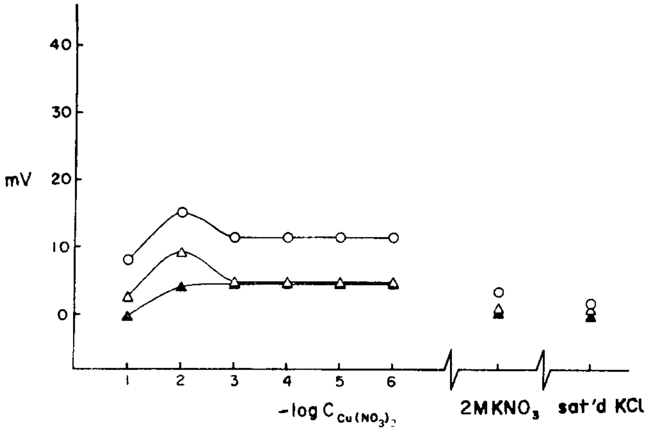


FIG. 4.—Calculated differences in liquid-junction potential between a bridge solution of $2M$ KNO_3 contacting copper and salt solutions and a bridge solution of

○ $1M$ $NaNO_3$
▲ $1M$ KNO_3
△ saturated KCl

contacting the same solutions. The ionic strength of the copper solutions was 0·3, obtained by addition of KNO_3.

should be a better choice than a bridge containing sodium nitrate. The Orion filling solution contains about $0{\cdot}7M$ potassium chloride, about $1{\cdot}5M$ potassium nitrate and small amounts of sodium and silver ions. Chloride ions form complexes with copper(II) ions and both the Orion filling solution and saturated potassium chloride are less suitable. The $2M$ potassium nitrate bridge solution has therefore been used throughout in the following and no calculated corrections for the liquid-junction potential have been applied.

The electrode surface

If the electrode surface contains cracks or pits the first sample solution will enter these. When the electrode is moved to a second sample solution the first will be displaced from the cracks only slowly. Different parts of the solid will be in contact with solutions of different concentrations. A mixed potential with a current path through the solid, the first sample solution, the main sample solution and back to the solid will be set up. The mixed potential will lie somewhere between what it should have been in the first and in the second solution. There will be a slow drift due to displacement of the first solution from the cracks. The Orion copper sulphide electrode has been studied with respect to influence from mixed potentials.

Figure 5 shows the electrode surface after two months use following delivery from the manufacturer, during which time the electrode had not been polished. Three types of spots can be recognized, linear pits, shallow diffuse pits with a rough bottom, and dark areas of various shapes with well-defined boundaries. Figure 6 shows the electrode surface after polishing with a diamond paste. The electrode was rinsed in distilled water before the picture was taken. Only spots of the third type can be seen on this picture. The spots were originally of light colour, but in the intense light of the microscope they turned black in a few minutes. A part of the surface shown in Fig. 6 was illuminated for some minutes with a small light cone covering only a part of the picture area. The aperture was then opened and the picture was taken. It can be seen that the illuminated spots of Fig. 6 are darker.

TABLE I.—TIME VARIATION OF THE POTENTIAL (mV), OF ORION CuS-ELECTRODE IN 0·01M $Cu(NO_3)_2$, MEASURED *vs.* A DOUBLE-JUNCTION REFERENCE ELECTRODE CONTAINING 2M KNO_3

Time, *min*	1	2	3	4	5	6
Untreated electrode *cf.* Fig. 5	+315·0	+316·0	+317·0	+318·0	+319·2	+320·2
Electrode treated with silicone oil	+316·0	+315·9	+316·0	+316·2	+316·5	+316·9
Polished electrode *cf.* Fig. 6	+315·2	+315·2	+315·2	+315·2	+315·2	+315·2
Polished electrode treated with silicone oil. $I = 0{\cdot}3$	+301·63	+301·83	+301·83	+301·83	+301·83	+301·83
Polished electrode etched in 0·1M EDTA *cf.* Fig. 10	+314·00	+313·70	+313·63	+313·47	+313·47	+313·47

Electrode stability

Table I shows the stability of the potential readings when the electrode was subjected to different pretreatments. The results show that filling the pits with oil improves the stability and removing most of the pits by polishing improves the stability further. The last row but one shows measurements on a polished electrode treated with silicone oil. The surface condition of the electrode seemed to be of paramount importance for the stability of the potential and for obtaining a stable reading within reasonable time.

Copper(II) ion activity

Activity coefficients for the calculations made in this paper were obtained from a computer programme of the type given by Lee.[5] A positive deviation was always found at 0·1*M* copper(II) nitrate both in the medium with varying ionic strength and in the medium with constant ionic strength, $I = 0{\cdot}3$. The measurements were therefore repeated with constant nitrate concentration, $[NO_3^-] = 0{\cdot}3M$, in order to test for a weak nitrate complex. The deviation from linearity decreased but the result was inconclusive with regard to the existence of a nitrate complex. The deviation may be caused by a change in the liquid-junction potential or an erroneous value of the activity coefficient. It is not possible at present to arrive at better values of the activity coefficients but work along the lines described by Bates and Alfenaar,[7] and Leyendekkers,[7] seems promising for the future.

Calculation of the slope and the intercept

Calibration curves were obtained for the electrode after it had been subjected to various forms of pretreatment. The calibration was made with copper(II) nitrate solutions and a double-junction reference electrode filled with 2*M* potassium nitrate.

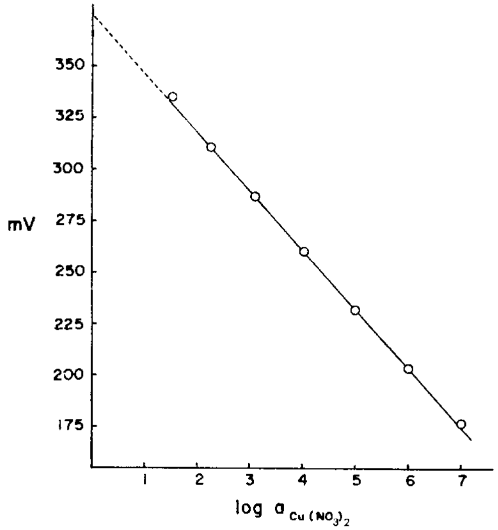
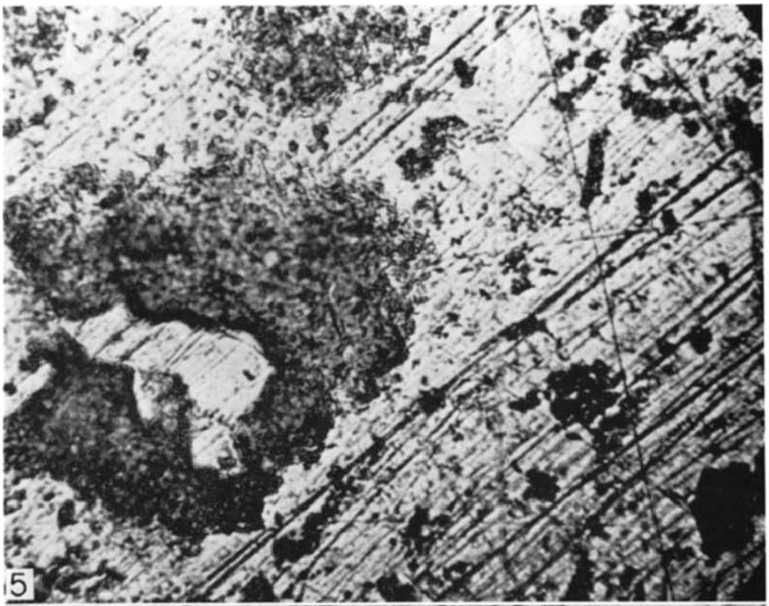


FIG. 7.—Calibration curve of a polished and silicone oil treated copper selective electrode in $Cu(NO_3)_2$ solutions with varying ionic strength. A double-junction reference electrode containing 2*M* KNO_3 was used.

The calibration curves were not strictly linear, as shown in Figs. 7 and 8. The measurement in 0·1*M* solution always resulted in a point above the line. Although this was the case a straight line was fitted to the points by using the least-squares method. This procedure will produce comparable values except for the EDTA-treated electrode. Evaluation was made over the range 10^{-1}–$10^{-6}M$ and the measurements were made in the order from lower to higher concentration. The temperature was always 23° which corresponds to a value of 29·38 mV/decade for $(RT \ln 10)/2F$.

The results of the measurements (Table II) confirm the conclusion drawn from the investigation of the drift. An electrode surface containing pits produces a line



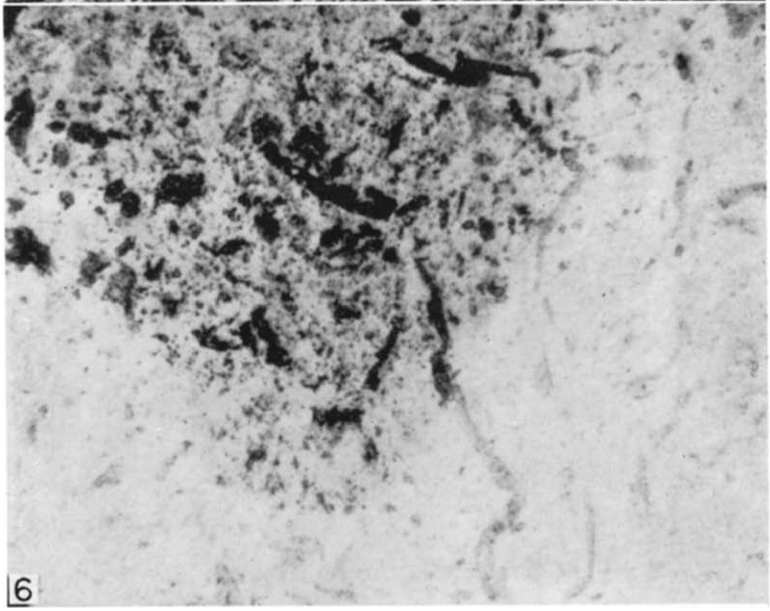


FIG. 5.—Photomicrograph of the surface of an Orion copper-selective electrode which had been in use for two months since purchase and not polished during that time. Magnification 724×.

FIG. 6.—Photomicrograph of the surface of a polished copper-selective electrode. The darker area had been illuminated for some minutes before the photograph was taken. Magnification 362×.

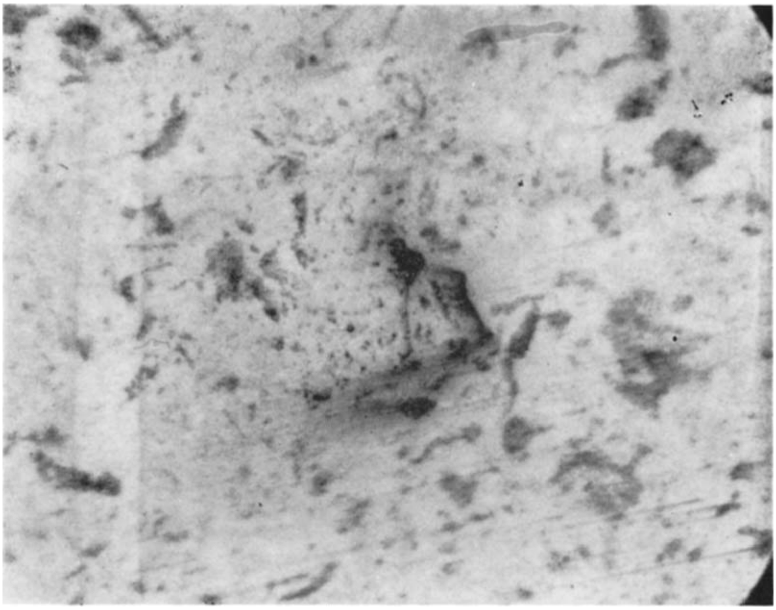


FIG. 10.—Photomicrograph of the surface of an copper-selective electrode etched for 50 hr in 0·1*M* EDTA. Magnification 362×.

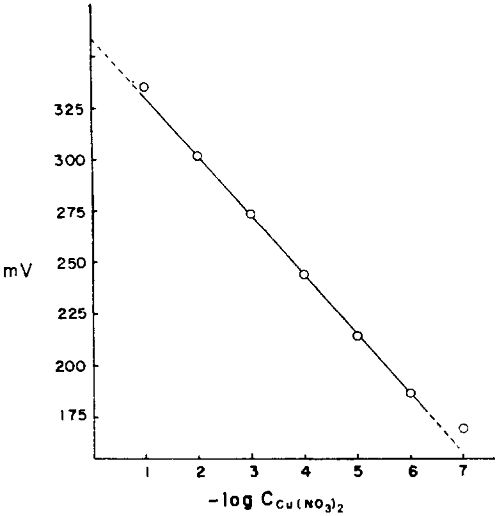


FIG. 8.—Calibration curve of a polished and silicone oil treated copper selective electrode in $Cu(NO_3)$ solutions with constant ionic strength, $I = 0{\cdot}3$, obtained by addition of KNO_3. A double-junction reference electrode containing $2M$ KNO_3 was used.

TABLE II.—SLOPE AND INTERCEPT, E' OF AN ORION CuS-ELECTRODE SUBJECTED TO VARIOUS PRETREATMENTS

	Varying ionic strength		Constant ionic strength	
	Slope, *mV/decade*	E', *mV*	Slope, *mV/decade*	E', *mV*
Untreated electrode *cf.* Fig. 5	16·2	370·2	—	—
Electrode treated with silicone oil	21·3	372·1	26·2	356·4
Polished electrode *cf.* Fig. 6	28·8	381·7	28·5	362·8
Polished electrode treated with silicone oil	29·2	378·2	29·6	362·7
Polished electrode etched in $0{\cdot}1M$ EDTA *cf.* Fig. 10	29·6*	382·8	—	—

* Slightly S-shaped calibration curve, probably due to residues of EDTA in the pits causing the points at $10^{-5}M$ and $10^{-6}M$ to fall below the line.

with a lower value of the slope than that of a polished electrode surface. The highest values of the slopes were obtained for a polished surface in which the remaining depressions were filled with silicone oil so that the penetration of solution into the material was reduced. This shows conclusively that surface irregularities produce a mixed electrode potential. The value of the slope of the EDTA-etched electrode is not comparable to the other values, because the calibration curve was S-shaped. A slope measured on the middle linear parts was lower (28·0 mV/decade) than that of a polished electrode. The measurements made on solutions with constant ionic strength were somewhat more reproducible than those for varying ionic strength.

The E' values depend on the long-term stability of the reference electrode. No checks were made to estimate this drift.

Electrode corrosion

Figures 9*a* and 9*b* show logarithmic plots of ionic activities at the copper electrode surface for solutions containing $10^{-1}M$ and $10^{-6}M$ Cu^{2+} respectively. The plots were made as described by Sillén.[4] Potentials are referred to the N.H.E. Below 0·31 V (Fig. 9*a*) or 0·15 V (Fig. 9*b*) respectively Cu^{2+} concentration decreases due to formation of Cu°. The concentration of S^{2-} due to dissolution of CuS is also shown. It is lower than that required for the reaction

$$S^{2-} \rightleftharpoons S + 2e^- \qquad E^\circ = -0{\cdot}48\ V$$

up to a redox potential of about 0·57 (Fig. 9*a*) or 0·42 V (Fig. 9*b*) respectively. At more oxidizing potentials CuS can be corroded if a suitable accelerating agent is present. Thermodynamically such an oxidation can be performed with nitrate ions but the reaction rate becomes appreciable only in strongly acid solutions. The same is true for perchloric acid and in this case the reaction rate in $0{\cdot}1M$ perchloric acid is so high that the response to Cu^{2+} is seriously impaired. Measurements in $1M$ sodium perchlorate could be carried out at pH 4–5, however. The corrosion was visible under the microscope. In nitrate solutions, $I = 0{\cdot}3$, an E–pH diagram could be obtained down to pH 2 and possibly lower.

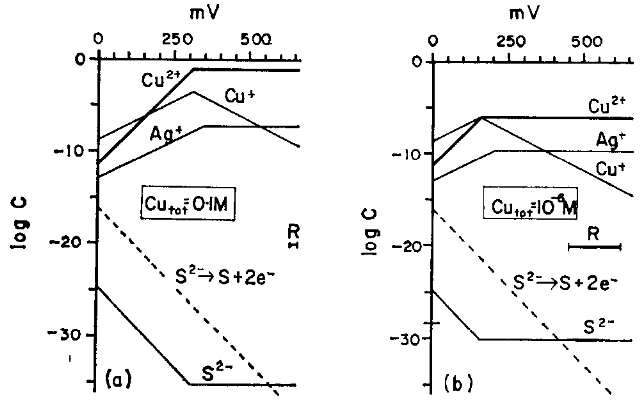


FIG. 9.—Logarithmic plots of some ion activities in equilibrium at the surface of a copper ion-selective electrode as a function of the redox potential *vs.* N.H.E. The equilibrium of oxidation of sulphide to sulphur is also shown. (*a*) Cu $0{\cdot}1M$; (*b*) Cu $10^{-6}M$.

The amount of Cu^+ can be neglected at a total copper concentration of the order of $0{\cdot}1M$ but this is not the case below a redox potential of 0·25 V in $10^{-6}M$ solutions. The redox potential of the copper(II) nitrate solutions used was determined by use of bright platinum electrodes. Two electrodes were used to check the reproducibility, which was rather poor. Two series were made, one at about pH 4 and the other at about pH 5·5. The ranges of redox potentials obtained are marked with R in the figure. The redox potential was so high that the presence of Cu^+ in the standard solutions could be neglected in all cases. The redox potentials of the calibration solutions were so high that oxidation of S^{2-} to S can take place readily, but the rate is probably very low or measurements in the most dilute solutions would have been impossible.

The electrode surface consists of a mixture of CuS and Ag_2S. If equilibrium is attained, the silver ion activity in the solution adjacent to the surface will be that shown in Fig. 9. When the solution is made more reducing, reduction of silver ions will occur before reduction of copper(II) ions to copper metal. Silver can also be formed under the influence of light. In order to study whether such a reaction interfered with the electrode function the surface of a polished dry electrode was illuminated with focused strong light for three hours. The slope and intercept were then determined and found to be identical to those for a newly polished electrode. Reduction of some of the silver ions to silver metal does not affect the electrode function.

Hansen, Lamm and Růžička[8] have shown that EDTA treatment of a sulphide-activated "Selectrode" improves the performance. They also reported that conditioning of commercial electrodes with EDTA, including the Orion electrode, did not produce significant effects. In order to study the conditioning effects on the electrode surface we have immersed the Orion electrode in stirred 0·1*M* EDTA at pH 4·5 for about 50 hr. A photomicrograph of the surface is shown in Fig. 10. The etching has produced diffuse pits with rounded contours. From the slope and intercept of this treated electrode (Table II) it is seen that this treatment is inferior to diamond polishing. The stability, as shown in Table I, is good but slightly less than that of a polished electrode treated with silicone oil.

Thomas and Williams[9] have shown that dislocations in solid surfaces possess enhanced reactivity and that etching is initiated at the dislocations. It is very likely that the attack on the copper electrode surface in corroding media also starts at dislocations. Spots of the first two types mentioned above, see Fig. 5, may be caused by this type of attack. As the etching was made under undefined conditions and mechanical scratches cannot be ruled out, no conclusions about the types of dislocations may be drawn. If this explanation is valid, a more perfect solid should make an electrode more resistant to chemical attack.

The etching rate in EDTA solutions is probably also greater at dislocations and will produce pits which cause mixed potentials. Preparation of the precipitate in the presence of EDTA according to Hansen, Lamm and Růžička will probably decrease the number of dislocations in the material. When the material is later pressed or rubbed into Teflon–graphite a compact solid more resistant to etching attacks will result. These authors also report a considerable improvement when the activated "Selectrode" was conditioned with EDTA. The surface of a Teflon–graphite electrode has probably quite different properties from those of the surface of a pressed pellet and these may arise from a lower formation of etch pits.

Some sulphide electrodes studied a year earlier had deep cracks around the edge where the electrode material was glued to the stem. These electrodes, of course, produced very erratic calibration curves with slopes between 10 and 20 mV/decade. The cracks were so large that inspection of an electrode with a magnifying glass revealed such defects in manufacture. Attempts to fill the cracks with paint or glue were unsuccessful.

Acknowledgement—The authors wish to thank Dr. M. Sharp for revising the English.

Zusammenfassung—Beim Gebrauch verschiedener Referenzelektroden wurden in Kupfer(II)-Lösungen Änderungen der Diffusionspotentiale gemessen. Neigung und Achsenabschnitt einer Eichkurve für eine kupfer-selektive Elektrode werden von der Auswahl der Referenzelektrode abhängen. Der Zustand der Elektrodenoberfläche einer kupfer-selektiven Elektrode von Orion wurde mikroskopisch untersucht und der Einfluß des Redoxpotentials auf die Korrosionsbeständigkeit der Elektrode diskutiert. Oxidierende Lösungen bilden Ätzgruben an Versetzungen im Material und es stellt sich ein Mischpotential an der Elektrode ein. Wenn die Oberfläche Ätzgruben enthält, sind Neigung, Beständigkeit und Ansprechgeschwindigkeit viel geringer. Es wurde gezeigt, daß Polieren mit Diamant die Elektrode beträchtlich verbessert.

Résumé—On a mesuré les changements dans les potentiels de jonction liquide dans des solutions de cuivre(II) quand différentes électrodes de référence sont utilisées. La pente et l'allure entre deux points d'une courbe d'étalonnage pour une électrode sélective du cuivre dépendront du choix de l'électrode de référence. On a étudié microscopiquement la condition de la surface d'électrode d'une électrode Orion sélective du cuivre, et l'on discute de l'influence du potentiel redox sur la stabilité de l'électrode vis-á-vis de la corrosion. Les solutions oxydantes produiront des cavités aux dislocations de la matière et il y aura un potentiel d'électrode mixte. La pente, la stabilité et la vitesse de réponse sont beaucoup plus faibles lorsque la surface contient des cavités. On a montré que le polissage au diamant améliore grandement l'électrode.

REFERENCES

1. M. Sharp and G. Johansson, *Anal. Chim. Acta*, 1971, **54**, 13.
2. J. W. Ross, Jr., in *Ion Selective Electrodes*, NBS Special Publ. No. 314, ed. R. A. Durst, Washington, 1969.
3. M. Sato, *Electrochim. Acta*, 1966, **11**, 361.
4. L. G. Sillén, in *Treatise on Analytical Chemistry*, Part I, Vol. 1, Chap. 8, ed. I. M. Kolthoff, P. J. Elving and E. B. Sandell, Interscience, New York, 1959.
5. T. S. Lee, *ibid.*, Chap. 7.
6. R. G. Bates and M. Alfenaar, in *Ion Selective Electrodes*, NBS Special Publ. No. 314, ed. R. A. Durst, Washington, 1969.
7. J. V. Leyendekkers, *Anal. Chem.*, 1971, **43**, 1835.
8. E. H. Hansen, C. G. Lamm and J. Růžička, *Anal. Chim. Acta*, 1972, **59**, 403.
9. J. M. Thomas and J. O. Williams, in *Progress in Solid-State Chemistry*, Vol. 6, ed. H. Reiss and J. O. McCaldin, Pergamon Press, Oxford, 1971.

Talanta, 1972, Vol. 19, pp. 1633 to 1638. Pergamon Press. Printed in Northern Ireland

INDIRECT ATOMIC-ABSORPTION DETERMINATION OF ppM LEVELS OF ARSENIC BY COMBUSTION OF AN MIBK EXTRACT OF ARSENOMOLYBDIC ACID

Y. YAMAMOTO, T. KUMAMARU, Y. HAYASHI, M. KANKE and A. MATSUI
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda, Hiroshima, Japan

(*Received* 13 *October* 1971. *Accepted* 24 *March* 1972)

Summary—An indirect atomic-absorption method for arsenic has been developed. Arsenic(III) is oxidized to arsenic(V) by iodine, then arsenomolybdic acid is formed and extracted into MIBK from 0·2–1·6*M* hydrochloric acid. Excess of molybdate is scrubbed from the organic phase, and then the molybdenum in the heteropoly acid is determined by its atomic absorption at 313·3 nm. Silicate and phosphate interfere. A procedure is described for determination of ppM levels of arsenic in water.

ALTHOUGH atomic-absorption spectrophotometry is commonly used for direct determination of metals, the method is not suitable for most non-metallic elements, because their resonance lines lie in the far ultraviolet, and various indirect methods are generally used, often coupled with a solvent extraction separation.

Several indirect methods based on heteropoly acid chemistry have been developed. Inorganic phosphate is determined by extracting phosphomolybdic acid into a suitable solvent and estimating the molybdenum content in the extract by means of atomic-absorption spectrophotometry.[1–4] Silicon,[3] vanadium[5] and niobium[6] are also determined indirectly by measuring the molybdenum content of the heteropoly acid.

Boltz *et al.*[7] have recently done the same for arsenic, extracting arsenomolybdic acid into methyl isobutyl ketone (MIBK), scrubbing with hydrochloric acid and water to remove excess of molybdate from the extract, then stripping the heteropoly acid into alkaline aqueous medium and determining the molybdenum.

We have found that direct nebulization of the MIBK extract into an air–acetylene or nitrous oxide–acetylene flame is satisfactory if the extract is properly scrubbed. The use of a larger aqueous/organic phase-volume ratio enhances the sensitivity by the enrichment effect, and MIBK is more efficiently nebulized than water. A determination of ppM levels of arsenic is described which has been successfully applied to various water samples.

EXPERIMENTAL

Reagents

All solutions were prepared from analytical-reagent grade chemicals and demineralized water, and stored in polyethylene bottles.

Standard arsenic(III) solution. Arsenious oxide (0·133 g) was dissolved in 10 ml of 0·1*M* sodium hydroxide, 5 ml of hydrochloric acid were added and the solution was diluted to 1000 ml to give a 100-ppm arsenic solution which was diluted to 5 ppm concentration before use.

Arsenic-76 solution. One mCi of arsenic ($HAsO_2$ in 1*M* hydrochloric acid) was diluted to a suitable concentration.

Iodine–potassium iodide solution. Potassium iodide (0·4 g) and iodine (0·25 g) were dissolved in 100 ml of water.

Potassium iodide solution, 15% w/v.

Sodium bicarbonate solution, 4·2% w/v.

Ammonium paramolybdate tetrahydrate solution, 10% w/v.

Stannous chloride dihydrate solution, 40% w/v, in hydrochloric acid. A small amount of metallic tin was added to prevent oxidation.

Metallic zinc. Granular zinc metal (1000–1410 μm) with arsenic content <0·01 ppm, washed with hydrochloric acid (1 + 10), then water, and dried before use.

Ferric chloride hexahydrate solution, 5% w/v in 0·6*M* hydrochloric acid.

Apparatus

A Nippon Jarrell-Ash Model AA-1 EW atomic-absorption spectrophotometer with a Westinghouse hollow-cathode molybdenum lamp. An Aloka Model PSM 801 γ-ray spectrometer equipped with a 1·5 × 1 in. NaI(Tl) crystal.

Procedure

Place 10 ml of solution, containing not more than 50 μg of arsenic(III), in a 125-ml separatory funnel and dilute to 50 ml. Add 1 ml of iodine solution, 4 ml of ammonium molybdate solution and 5 ml of conc. hydrochloric acid (final acidity ~1·2*N*). After 5 min, add 10 ml of MIBK and shake the funnel vigorously for 3 min with a mechanical shaker. Allow to stand for about 15 min, and discard the aqueous layer. Wash the MIBK layer with 10 ml of hydrochloric acid (1 + 10). Repeat the washing with 10 ml of hydrochloric acid (1 + 10) at least four times to remove excess of molybdate. Measure the absorption of the molybdenum at 313·3 nm against a reagent blank, under the optimum operating conditions of the instrument, using an air–acetylene flame.

Procedure for water analysis

Place the sample solution (containing up to 5 μg of arsenic) in a conical beaker, add 3 ml of sulphuric acid (1 + 9) and 1 ml of ferric chloride solution per litre of the sample solution. Heat on a water-bath at 70–80° and neutralize with ammonia solution (1 + 3) to pH 9–10 (*m*-Cresol Purple). Cool, filter (*e.g.*, Toyo Roshi paper No. 5A), and dissolve the precipitate in 2–10 ml of warm hydrochloric acid (1 + 1) into a 50 ml conical flask (Fig. 1), washing the filter paper with a small portion of water. Keep the total volume of the aqueous solution to <25 ml. Add 2 ml of potassium iodide solution and 1 ml of stannous chloride solution, let stand for 15–30 min, quickly add 2 g of granular zinc, immediately insert the stopper and let the gases bubble through a mixture of 1 ml of the iodine solution and 0·2 ml of the sodium bicarbonate solution, for one hour at room temperature. Transfer

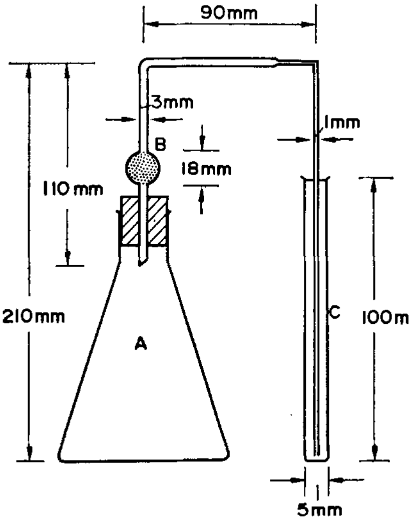


FIG. 1.—Apparatus for evolution of arsine. A Erlenmeyer flask (50 ml); B glass wool impregnated with lead acetate; C absorption tube.

the absorption solution to a 125-ml separatory funnel, dilute it to 50 ml with water, and continue according to the general procedure described above, using a nitrous oxide–acetylene flame to increase the sensitivity.

RESULTS AND DISCUSSION

Oxidation

Arsenic(III) does not form a heteropolymolybdate, and iodine was selected to oxidize it to arsenic(V). A pH between 0·5 and 6 was found necessary for quantitative formation of arsenomolybdic acid, and an acidity of 0·2–1·6*M* hydrochloric acid for quantitative extraction from 0·2–6*M* hydrochloric acid. The degree of extraction rapidly decreases with acid concentrations less than 0·2*N*, suggesting incomplete formation of arsenomolybdic acid. When the acidity is >1·6*N*, the reagent blank increases with acidity, presumably because of the extraction of the isopolymolybdate formed. The acidity was therefore set at approximately 1·2*M* with respect to hydrochloric acid.

Molybdate concentration

Addition of 0·2–0·5 g of ammonium molybdate was adequate for complete extraction of the heteropoly acid. Addition of more led to positive errors, because the 6-ml excess was then not completely removed by washing, unless further washing was done.

Acidity and number of washings

The effect of the number of washings is shown in Fig. 2. Ten-ml portions of hydrochloric acid (1 + 10) were shaken with 10-ml portions of the extract, and the molybdenum content in each phase was determined by atomic absorption. The results indicate that the excess of molybdenum was completely removed by washing at least three times.

In alkaline or neutral solutions arsenomolybdic acid may decompose, while from acidic solution the isopolymolybdate is appreciably extracted. The effect of

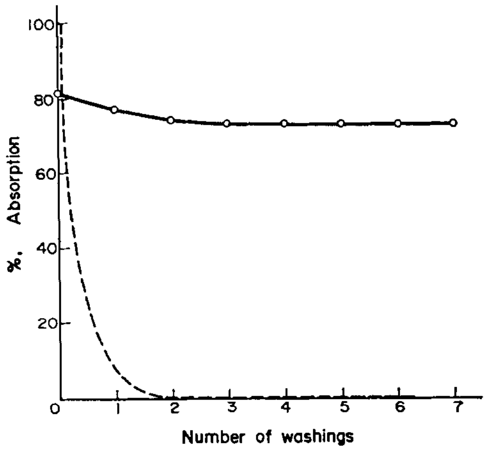


FIG. 2.—Effect of number of washings with hydrochloric acid (1 + 10) for 50 μg of arsenic: 1: Organic phase, 2. washing solution. Reference for 1, reagent blank; reference for 2, hydrochloric acid (1 + 10) saturated with MIBK.

acidity at two concentrations of arsenic is shown in Fig. 3. For a single washing with equal phase volumes, an acidity of 0·2–1·6*M* hydrochloric acid was found to give a plateau on the absorption *vs.* pH graph.

Recovery of arsenic

MIBK is more efficiently nebulized than water, so the sensitivity for molybdenum in the organic phase is higher than that for the aqueous phase. Therefore, it was not certain from the experiments described above whether appreciable loss of arsenic occurred. This point was tested by using ^{76}As as tracer, and as Table I shows, oxidation by iodine was complete and loss of arsenic in the extraction procedure was negligible.

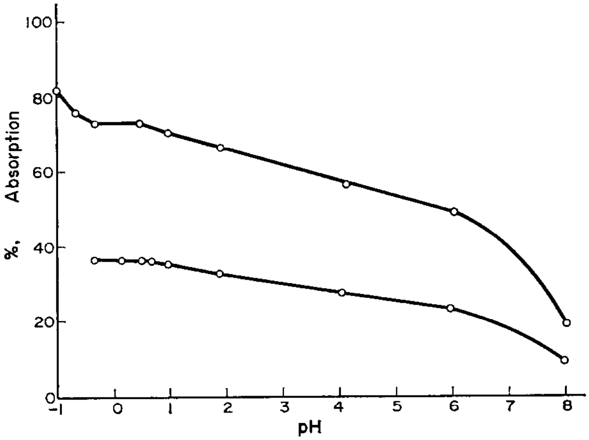


FIG. 3.—Effect of acidity on washing. 1 : 50 μg of arsenic, 2 : 25 μg of arsenic. 10 ml of MIBK, 10 ml of washing solution; reference, reagent blank.

TABLE I.—RECOVERY OF ARSENIC (1 ppm LABELLED WITH ^{76}As)

Number of washings	Degree of extraction of As, %
0	99·8 ± 0·1
1	99·8 ± 0·3
2	99·6 ± 0·4
3	99·5 ± 0·4
4	98·8 ± 0·4

The shaking time for the extraction was varied from 0·5 to 10 min. It was found that 2 min shaking sufficed for equilibration in the extraction. Shaking for 1 min was found to be sufficient for each washing.

Choice of solvent

Various ketones, alcohols and esters were tested as extractants. Arsenomolybdic acid was well extracted by ketones (MIBK, *etc*) and alcohols (*e.g.*, n-butanol and n-pentanol) but not by esters. MIBK was selected because of the enhancement of sensitivity by its more efficient nebulization.

It was found that the apparent sensitivity increased with increasing volume-ratio of aqueous to organic phase (Fig. 4), owing to the solubility of MIBK in water causing a decrease in volume of the organic phase.

Calibration curves and precision

Beer's law is obeyed up to 1 ppm of arsenic and the sensitivity for 1 % absorption was 0·01 ppm of arsenic. For 10 solutions, each containing 1 ppm of arsenic, the mean scale reading (% absorption) was 73, with a relative standard deviation of 3 %.

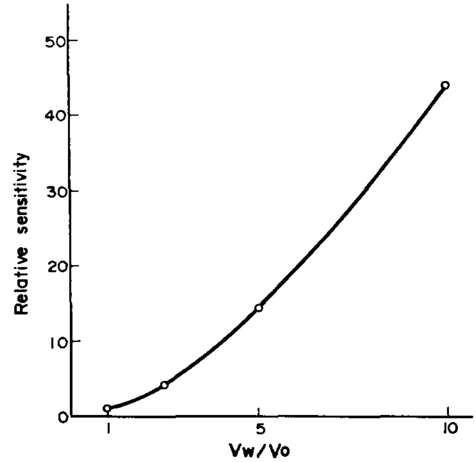


FIG. 4.—Effect of the volume ratio on sensitivity. 50 μg of arsenic; 10 ml of MIBK; reference, reagent blank.

Temperature fluctuations (15–25°) had no effect. A nitrous oxide–acetylene flame gave approximately ten times the sensitivity obtained with an air–acetylene flame. Thus, if a larger phase-volume ratio such as 20:1 is also used, 0·1 ppM of arsenic can be determined.

Selectivity

Large amounts of sodium, potassium, magnesium, calcium, aluminium, tin(II), lead, chromium(III), manganese(II), cobalt, zinc, cadmium, mercury(II), chloride, bromide, nitrate, sulphate, perchlorate and permanganate do not interfere. Antimony(III), silicate, phosphate, tungstate, vanadate and dichromate interfere (Table II). Phosphomolybdic and silicomolybdic acids are well extracted into MIBK and give positive errors. The others give large negative errors when present in similar amounts to arsenic, possibly by formation of mixed or competing heteropoly

TABLE II.—INTERFERENCE EFFECTS ON 1 ppm OF ARSENIC

Element	Added as	Concentration producing ±3 % error, *ppm*
Antimony(III)	Chloride	1
Iron(III)	Iron alum	50
Vanadium(V)	Ammonium vanadate	0·5
Chromium(VI)	Potassium dichromate	1
Tungsten(VI)	Sodium tungstate	0·5
Phosphorus	Ammonium phosphate	0·2
Silicon	Sodium silicate	0·2

TABLE III.—ANALYSIS OF WATERS

Sample	Arsenic, *ppM*	
	Spectrophotometric method	Proposed method
River water A	7	8
River water B	*	*
Waste water A	38	37
Waste water B	32	40
Waste water C	37	38
Sea-water (waste) A	44	44
Sea-water (waste) B	17	17
Sea-water (waste) C	5	6
Sea-water A	*	*
Sea-water B†	99	100

* Not detected.
† Sea-water A containing 100 ppM of arsenic.

acids which make the amount of molybdenum not equivalent to the amount of arsenic present.

Application to water analysis

Arsenic must be separated from phosphate and silicate, which can be done by co-precipitation with ferric hydroxide. The arsenic is then evolved as arsine and oxidized to arsenic(V). As a check, samples were also analysed by the silver–diethyldithiocarbamate–brucine–chloroform spectrophotometric method (a modification of the silver–diethyldithiocarbamate–pyridine method.)[8] The results are shown in Table III. It is seen that both sets of results are in satisfactory agreement.

Zusammenfassung—Eine indirekte Arsen-Bestimmungsmethode durch Atomabsorption wurde entwickelt. Arsen(III) wird durch Jod zu Arsen(V) oxidiert, dann Arsenomolybdänsäure gebildet und aus 0,2–1,6*M* Salzsäure in MIBK extrahiert. Der Überschuß von Molybdat wird aus der organischen Phase ausgewaschen und dann das Molybdän in der Heteropolysäure mit Hilfe seiner Atomabsorption bei 313,3 nm bestimmt. Silikat und Phosphat stören. Ein Verfahren zur Bestimmung von ppm-Mengen Arsen in Wasser wird beschrieben.

Résumé—On a élaboré une méthode indirecte d'absorption atomique pour l'arsenic. On oxyde l'arsenic(III) en arsenic(V) par l'iode, puis on forme l'acide arsénomolybdique et l'extrait en méthylisobutylcétone (MIBK) d'une solution 0,2–1,6*M* d'acide chlorhydrique. L'excès de molybdate est lavé de la phase organique, puis l'on dose le molybdène dans l'hétéropoly acide par son absorption atomique à 313,3 nm. Le silicate et le phosphate gênent. On décrit une méthode pour le dosage de ppm d'arsenic dans l'eau.

REFERENCES

1. T. Kumamaru, Y. Otani and Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1967, **40**, 429.
2. W. S. Zaugg and R. J. Knox, *Anal. Chem.*, 1966, **38**, 1759.
3. G. F. Kirkbright, A. M. Smith and T. S. West, *Analyst*, 1967, **92**, 411.
4. T. R. Hurford and D. F. Boltz, *Anal. Chem.*, 1968, **40**, 379.
5. R. J. Jakubiec and D. F. Boltz, *Anal. Letters*, 1968, **1**, 347.
6. G. F. Kirkbright, A. M. Smith and T. S. West, *Analyst*, 1968, **93**, 292.
7. R. S. Danchik and D. F. Boltz, *Anal. Letters*, 1968, **1**, 901.
8. *Japan Industrial Standards* K 0101, 1966.

Talanta, 1972, Vol. 19, pp. 1639 to 1644. Pergamon Press. Printed in Northern Ireland

SHORT COMMUNICATIONS

Determination of small amounts of water with coulometrically generated Karl Fischer reagent

(*Received* 1 *May* 1972. *Accepted* 23 *May* 1972)

FOR THE DEVELOPMENT and improvement of many industrial processes, it is often necessary to be able to determine very small amounts of water in a variety of substances. A large number of methods have been reported including some based on infrared[1,2] and gas chromatographic[3-6] procedures. In general these methods apply only to the determination of water in solutions and only a few methods have been proposed for water in solids, of which different forms of titration with the Karl Fischer (KF) reagent[7,8] and electrolysis of water in cells of the Keidel type[9] are the most widely applicable. For the smaller amounts of water, these methods give errors of a few per cent. Besides, a large number of substances interfere and cause erroneous results.

In a previous paper,[10] we presented a method based on the coulometric generation of iodine at controlled potential. This method has now been improved. The electrolysis cell has been reconstructed and equipped with clay filters instead of glass frits. The electronic circuitry is fitted with a booster which makes it possible to draw considerably higher currents and the integrator is furnished with a digital read-out. These improvements have resulted in shorter analysis times, better accuracy and an increased range of determination (0·005–5 mg of water). A moveable oven system connected to the nitrogen inlet of the electrolysis cell has extended the field of applications to include the determination of water of absorption, adsorption and hydration, both in inorganic and organic solids. As the samples are not in direct contact with the solution, substances which otherwise could interfere with the KF reagent can also be analysed.

EXPERIMENTAL

Apparatus

Electrolysis cell. A cross-section of the redesigned electrolysis cell is shown in Fig. 1. The nitrogen inlet is through the Teflon B5 socket (A) and a Teflon tube with Swagelock connection (B). The working electrode (C) is a circular platinum-gauze, which is firmly fixed at the end of a shaft coated with Teflon and running in two 3 × 10 mm stainless-steel ball-bearings (F). Two Haldenvanger clay filters (D) (W. Haldenvanger, Berlin 20) separate the counter-electrode (E) from the working electrode. The pore size of these clay filters is about a fifth that of glass frits of porosity 4 and the electrical conductivity of the clay filters is also much smaller. Consequently, electrolysis with larger currents can be carried out. The clay filters are, however, rather fragile and difficult to fix to the glass walls. A special cement supplied by Haldenvanger must often be used to get sufficiently good sealing between glass and filter. Electrodes and solutions are as described earlier.[10]

Oven system. An outline of the oven system with electrolysis cell is shown in Fig. 2. The oven is made of aluminium, insulated with asbestos, and heated by two 100-mm long heaters. Temperatures up to 500° can be obtained and are measured with a platinum–platinum/rhodium thermocouple. The Pyrex glass tube has an inner diameter of 8 mm, a B10 joint and nitrogen inlet connections.

Electronic circuitry. Some improvements in the electronic circuitry described earlier have been made. The potentiostat has been fitted with a booster (see Fig. 3) capable of supplying larger electrolysis currents.

The integrating resistor of 1 MΩ is replaced by a series of eight changeable resistors ranging from 0·2 to 5 MΩ in order to cover the whole range of determinations more accurately. Each resistor is separately calibrated together with the capacitor by time and voltage measurements. The read-out device for the integrator, earlier a compensation bridge, is now a digital voltmeter (Model 404 Tyco Instrument Division) which gives a faster and more accurate presentation.

Determination of water in solids

A sample in an aluminium boat is placed in the glass tube and the oven is put into the forward position. During the sample heating, a calculated excess of iodine is generated. A nitrogen stream

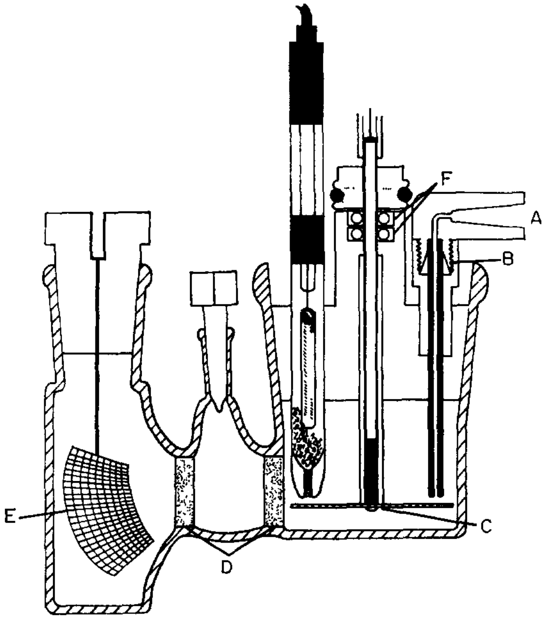


Fig. 1.—Electrolysis cell.
- A. Teflon B5 socket
- B. Swagelock connection
- C. Rotating working electrode
- D. Clay filters
- E. Counter electrode
- F. Stainless-steel ball-bearings

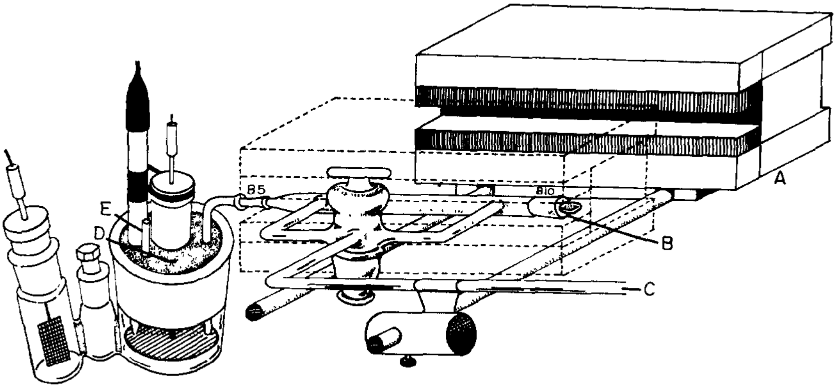


Fig. 2.—Oven system with electrolysis.
- A. Moveable asbestos-coat aluminium oven block
- B. Pyrex glass tube
- C. Nitrogen inlet
- D. Nitrogen outlet
- E. Teflon stopper

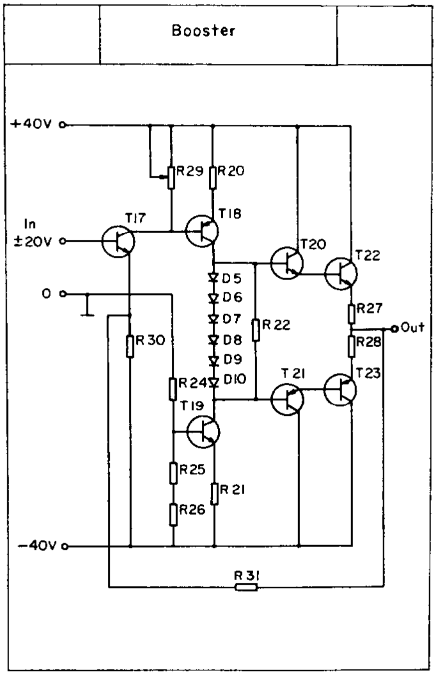


FIG. 3.—Booster

List of components

R 20, 21 = 150 ohm
R 22 = 1 kohm
R 24 = 39 kohm
R 25 = 180 ohm
R 26 = 560 ohm
R 27, 28 = 47 ohm
R 29 = 5 kohm
R 30, 31 = 82 kohm

D 5–D 10 = BA 127
T 17 = BC 107
T 18, 21 = RCA 40362
T 19, 20 = RCA 40348
T 22 = 2 N 3767
T 23 = 2 N 3741

at a rate of 5–25 ml/min (depending on heating temperature and kind of sample) carries the liberated water into the electrolysis cell. The reduction of the iodine excess is started after 3–7 min heating of the sample and, when the reduction is completed, the oven is moved to the rear and the glass tube is cooled with compressed air. To ensure completeness of analysis, a blank test is performed between every sample analysis. If the blank test gives too high a read-out, some more blank tests must be done until a stable result is reached. Accordingly, before the next analysis, the nitrogen stream and/or the heating temperature must be increased.

RESULTS AND DISCUSSION

Stock solutions were prepared from "dry" methanol by the addition of known amounts of water. All handling was under a dry nitrogen atmosphere. The water content in the "dry" methanol was, however, first determined both by the standard-addition technique and by direct analysis of 0·5-ml samples added to the electrolysis cell by Agla syringe. The results obtained by the two methods agreed very well. Series of samples were then prepared from the stock solutions and the results of such a series are shown in Table I. The most favourable range for the apparatus is 0·01–5 mg of water (rel. std. devn. $< 0{\cdot}3\,\%$). It is of course possible to determine larger amounts of water, but it will take rather a long time to generate the amount of iodine required and also to reduce the excess (15–25%), which will influence the accuracy. Besides, conventional KF methods work rather well for solutions containing more than 5 mg of water.

Smaller amounts of water than 0·01 mg have been determined in several organic liquids, but for the sake of simplicity, the presentation is restricted to water determined in methanolic solutions, as the technique is similar for other solutions.

TABLE I.—COULOMETRIC DETERMINATION OF WATER IN METHANOL

H_2O calculated, *μg*	H_2O found, *μg*	No. of determinations	Standard deviation, *μg*	Rel. standard deviation, %
0·56	0·60	4	0·07	11·6
1·41	1·43	4	0·05	3·5
2·82	2·75	4	0·04	1·5
4·50	4·48	4	0·04	0·8
5·63	5·62	4	0·04	0·7
10·11	10·09	4	0·03	0·3
50·56	50·61	4	0·10	0·2
101·1	101·0	3	0·14	0·1
500·4	499·9	3	0·31	0·06
1001	1002	3	0·6	0·06
5004	5007	3	4	0·08

The determination limit for a quantitative analysis is defined by Currie[11] as the amount for which a relative standard deviation of 10% is expected. This value is obtained in this case for about 0·75 μg. One limiting factor is the slow reaction between KF reagent and water at these low concentrations, and it is necessary to generate up to a tenfold excess of iodine to get complete reaction, which necessitates relatively long analysis times and accordingly large blank corrections. Experiments with *N*-ethylpiperidine used as a catalyst to increase the rate of reactions as proposed by Archer and Jeater[12] gave no observable improvement. Another limiting factor is the great difficulty in handling samples. It is very difficult to keep these low concentrations of water in the samples constant. Small drifts in the values, day to day, could not be avoided.

In many cases, when maximum accuracy is not required, the times of analysis can be shortened considerably. The principle for an accurate determination at controlled potential is that the reduction is allowed to proceed until the residual current results in only a small and reproducible integrator read-out (1–2 mV/min). As the last part of the reduction takes most of the time, some minutes can be saved if the reduction stops when the read-out is about 10 mV/min, but in this case the uncertainty of the determination will of course increase.

TABLE II.—DETERMINATION OF WATER IN SOME HYDRATES

Substance	Moles of H_2O	No. of determinations	Std. deviation, *mole*
(Weight 0·2–1 mg*)			
Oxalic acid ($2H_2O$)	1·994	6	0·004
Disodium tartrate ($2H_2O$)	1·999	8	0·004
Barium chloride ($2H_2O$)	1·986	6	0·004
Copper sulphate ($5H_2O$)	4·992	8	0·005
Potassium alum ($12H_2O$)	11·989	5	0·004
(Weight 1–5 mg†)			
Oxalic acid ($2H_2O$)	1·996	8	0·004
Disodium tartrate ($2H_2O$)	1·999	11	0·003
Barium chloride ($2H_2O$)	1·985	15	0·003
Copper sulphate ($5H_2O$)	4·990	10	0·005
Potassium alum ($12H_2O$)	11·985	9	0·005

* Sartorius electronic ultramicrobalance 4125.

† Mettler microbalance M5.

Water in solids has been determined by the oven method described earlier. Table II gives results for the determination of water of hydration in some salts. It can be seen that the barium chloride contains somewhat smaller amounts of water than expected from the formula. According to Duval,[13] this is due to the fact that the salt is a mixture of the mono- and dihydrate. Consequently, the salt should not be employed as a standard in aquametry. The oxygen content in the salt[14] was in very good agreement with the results obtained here.

The water content of the copper sulphate pentahydrate was also determined by preparing methanolic solutions of 15–40 mg of the salt in volumetric flasks and then adding samples (50–100 μl) directly to the cell with an Agla syringe. With normal composition of the KF reagent, the analysis of copper sulphate pentahydrate will result in only 4·5 moles of water as reported by Mitchell *et al.*,[15] because of the reaction:

$$Cu(II) + I^- \rightarrow Cu(I) + 1/2\,I_2$$

If a very low iodine concentration (below 0·01M) and rather high sulphur dioxide concentration (more than 0·1M) are used, a reagent is obtained which gives a very slow reaction with the copper(II), allowing the $5H_2O$ of crystallization to be determined without interference. Blanks must be taken between every analysis to indicate whether any interference from the copper(II)–iodide reaction will arise. We found, for the pentahydrates, 4·996 moles of water per mole of copper with a standard deviation of 0·005 mole (25 determinations); the analysis times were 250–300 sec.

Replacing the oven with a high-temperature furnace and a quartz tube enables substances with very firmly bound water to be analysed, e.g., metal alloys with water contents in the range 1–5 ppm w/w. Temperatures up to 1200° can be obtained if necessary and the accuracy of the determinations is very satisfactory.

Experiments with a more automated method, some kind of air-locks for the electrolysis cell and tests of modified KF reagents are just some of the more urgent improvements being prepared.

Acknowledgement—The author thanks Professor K. J. Karrman for valuable help and discussions, Dr. Peter Sellers for correcting the English and the Swedish Board for Technical Development for financial support.

RONALD KARLSSON

Department of Analytical Chemistry
Chemical Center
University of Lund
S 220 07 *Lund 7, Sweden*

Summary—A coulometric method for the determination of small amounts of water described in a previous report has been further developed. Improved electronic circuitry and a redesigned electrolysis cell have extended the range of determination and decreased the time of analysis. By means of a movable oven specially adapted to the cell, water in solids has also been determined. The method presented is applicable with high accuracy in the range 0.005–5 mg of water in a large variety of substances.

Zusammenfassung—Ein in einer früheren Arbeit beschriebenes coulometrisches Verfahren zur Bestimmung kleiner Wassermengen wurde weiter entwickelt. Verbesserte elektronische Schaltungen und eine neu konstruierte Elektrolysezelle haben die Anwendungsmöglichkeiten des Verfahrens erweitert und die Analysenzeit vermindert. Mit Hilfe eines der Zelle besonders angepaßten beweglichen Ofens wurde auch Wasser in festen Stoffen bestimmt. Die angegebene Methode läßt sich mit hoher Genauigkeit im Bereich 0,005–5 mg Wasser in einer großen Anzahl verschiedener Stoffe anwenden.

Résumé—Une méthode coulométrique pour le dosage de petites quantités d'eau décrite dans un mémoire antérieur a été développée davantage. Un circuit électronique amélioré et une cellule d'électrolyse reconçue ont étendu le domaine de dosage et réduit le temps d'analyse. Au moyen d'un four mobile spécialement adapté à la cellule, on a également déterminé l'eau dans les solides. La méthode présentée est applicable avec une haute précision au domaine 0,005–5 mg d'eau dans une grande variété de substances.

REFERENCES

1. J. W. Forbes, *Anal. Chem.*, 1962, **34**, 1125.
2. S. T. Abrams and V. N. Smith, *ibid.*, 1962, **34**, 1129.
3. H. S. Knight and F. T. Weiss, *ibid.*, 1962, **34**, 749.
4. R. Kaiser, *Chromatographia*, 1969, **2**, 453.
5. O. L. Hollis and W. V. Hayes, *J. Gas Chromatog.*, 1966, **4**, 235.
6. J. M. Hogan, R. A. Engel and H. F. Stevenson, *Anal. Chem.*, 1970, **42**, 249.
7. J. Mitchell Jr. and D. M. Smith, *Aquametry*, Interscience, New York, 1948.

8. E. L. Bastin, Herbert Siegel and A. B. Bullock, *Anal. Chem.*, 1959, **31**, 467.
9. F. A. Keidel, *ibid.*, 1959, **31**, 2043.
10. R. Karlsson and K. J. Karrman, *Talanta*, 1971, **18**, 459.
11. L. A. Currie, *Anal. Chem.*, 1968, **40**, 586.
12. E. E. Archer and H. W. Jeater, *Analyst*, 1965, **90**, 351.
13. C. Duval, *Anal. Chim. Acta*, 1955, **13**, 32.
14. K. J. Karrman and R. Karlsson, *Talanta*, 1972, **19**, 67.
15. J. Mitchell Jr., D. M. Smith, E. C. Ashby and W. M. D. Bryant, *J. Am. Chem. Soc.*, 1941, **63**, 2927.

Talanta, 1972, Vol. 19, pp. 1644 to 1647. Pergamon Press. Printed in Northern Ireland

Studies on the extraction and determination of metals—I

Extraction of hafnium into methyl isobutyl ketone and tributyl phosphate

(*Received* 30 *March* 1971. *Revised* 10 *December* 1971. *Accepted* 15 *January* 1972)

ALTHOUGH there are many reports[1–18] on the extraction of hafnium from nitric acid alone or mixed with other acids, by TBP with xylene, kerosine or heptane as a diluent, little information can be found in the literature on the extraction of hafnium from different acids with MIBK or from hydrochloric acid with TBP–benzene solutions. The effect of various factors on such extractions was examined in the present work.

EXPERIMENTAL

Reagents

Standard hafnium solution. Hafnium dioxide (>99% purity), about 1 g, was dissolved by heating in 40 ml of a mixture (40:1) of nitric and hydrofluoric acids. Ammonia solution was added to precipitate the hydroxide, which was filtered off on paper, washed thoroughly with distilled water, and dissolved at once in dilute hydrochloric acid. Precipitation and dissolution were repeated several times and the final precipitate was dissolved in 5*M* hydrochloric acid. The concentration of hafnium in this solution was determined by gravimetry.[19]

Radioactive hafnium solution. $^{175+181}$Hf solution of about 1 mCi activity was diluted to 100 ml with 5*M* hydrochloric acid.

Hafnium solution (<*1 mg/ml*). Radioactive hafnium solution of about 10 μCi activity was added to various volumes (Hf < 50 mg) of the standard hafnium solution and mixed thoroughly, then ammonia solution was added to precipitate the hydroxide. The precipitate was collected on paper, washed thoroughly with water, and dissolved in the desired acid. The precipitation and dissolution were repeated several times and the final precipitate was dissolved in 50 ml of 5*M* acid.

Other reagents used were all of analytical-reagent grade.

Extraction procedure

Ten ml of an acid solution containing a 1·00-ml aliquot of the hafnium solution were shaken vigorously for a desired time (240 shakes/min) with an equal volume of MIBK or TBP–benzene in a 50-ml separatory funnel. When the two phases had separated, equal aliquots of each were transferred into polyethylene tubes. The gamma-activity of the $^{175+181}$Hf in each aliquot was counted by means of a scintillation counter (1080 V, discrimination 42·5 V). No temperature control was exercised but the ambient temperature was fairly constant at 20 ± 3°.

RESULTS AND DISCUSSION

Effect of various factors on the distribution ratio

Shaking time. With MIBK, equilibrium was found to be reached within 30 sec, irrespective of the acid used. Therefore, shaking for 1 min was adopted. In extraction with TBP, at least 20 min were needed to reach equilibrium with 6*M* hydrochloric acid medium, though 10 min sufficed for 7*M* hydrochloric acid and 9*M* nitric acid, and shaking for 30 min was adopted.

8. E. L. Bastin, Herbert Siegel and A. B. Bullock, *Anal. Chem.*, 1959, **31**, 467.
9. F. A. Keidel, *ibid.*, 1959, **31**, 2043.
10. R. Karlsson and K. J. Karrman, *Talanta*, 1971, **18**, 459.
11. L. A. Currie, *Anal. Chem.*, 1968, **40**, 586.
12. E. E. Archer and H. W. Jeater, *Analyst*, 1965, **90**, 351.
13. C. Duval, *Anal. Chim. Acta*, 1955, **13**, 32.
14. K. J. Karrman and R. Karlsson, *Talanta*, 1972, **19**, 67.
15. J. Mitchell Jr., D. M. Smith, E. C. Ashby and W. M. D. Bryant, *J. Am. Chem. Soc.*, 1941, **63**, 2927.

Talanta, 1972, Vol. 19, pp. 1644 to 1647. Pergamon Press. Printed in Northern Ireland

Studies on the extraction and determination of metals—I

Extraction of hafnium into methyl isobutyl ketone and tributyl phosphate

(*Received* 30 *March* 1971. *Revised* 10 *December* 1971. *Accepted* 15 *January* 1972)

ALTHOUGH there are many reports[1–18] on the extraction of hafnium from nitric acid alone or mixed with other acids, by TBP with xylene, kerosine or heptane as a diluent, little information can be found in the literature on the extraction of hafnium from different acids with MIBK or from hydrochloric acid with TBP–benzene solutions. The effect of various factors on such extractions was examined in the present work.

EXPERIMENTAL

Reagents

Standard hafnium solution. Hafnium dioxide (>99% purity), about 1 g, was dissolved by heating in 40 ml of a mixture (40:1) of nitric and hydrofluoric acids. Ammonia solution was added to precipitate the hydroxide, which was filtered off on paper, washed thoroughly with distilled water, and dissolved at once in dilute hydrochloric acid. Precipitation and dissolution were repeated several times and the final precipitate was dissolved in $5M$ hydrochloric acid. The concentration of hafnium in this solution was determined by gravimetry.[19]

Radioactive hafnium solution. $^{175+181}$Hf solution of about 1 mCi activity was diluted to 100 ml with $5M$ hydrochloric acid.

Hafnium solution ($<$*1 mg/ml*). Radioactive hafnium solution of about 10 μCi activity was added to various volumes (Hf < 50 mg) of the standard hafnium solution and mixed thoroughly, then ammonia solution was added to precipitate the hydroxide. The precipitate was collected on paper, washed thoroughly with water, and dissolved in the desired acid. The precipitation and dissolution were repeated several times and the final precipitate was dissolved in 50 ml of $5M$ acid.

Other reagents used were all of analytical-reagent grade.

Extraction procedure

Ten ml of an acid solution containing a 1·00-ml aliquot of the hafnium solution were shaken vigorously for a desired time (240 shakes/min) with an equal volume of MIBK or TBP–benzene in a 50-ml separatory funnel. When the two phases had separated, equal aliquots of each were transferred into polyethylene tubes. The gamma-activity of the $^{175+181}$Hf in each aliquot was counted by means of a scintillation counter (1080 V, discrimination 42·5 V). No temperature control was exercised but the ambient temperature was fairly constant at 20 ± 3°.

RESULTS AND DISCUSSION

Effect of various factors on the distribution ratio

Shaking time. With MIBK, equilibrium was found to be reached within 30 sec, irrespective of the acid used. Therefore, shaking for 1 min was adopted. In extraction with TBP, at least 20 min were needed to reach equilibrium with $6M$ hydrochloric acid medium, though 10 min sufficed for $7M$ hydrochloric acid and $9M$ nitric acid, and shaking for 30 min was adopted.

TBP concentration. Plots of log D *vs.* log C_{TBP} for hafnium extraction from 7 or 10M hydrochloric acid into TBP-benzene solution of various concentrations gave curves that had a slope of 2 for their linear portions. For 10M hydrochloric acid medium, log D was about 2 for TBP concentrations from 0·05 to 3·75M, indicating that quantitative extraction (>99%) of hafnium would be possible under these conditions. With TBP concentrations above 2M a longer time was needed for separation of the phases after shaking, so 1M TBP in benzene was used as the extractant in further work.

Acid concentration. The relationship between the distribution ratio and the acid concentration is shown in Fig. 1.

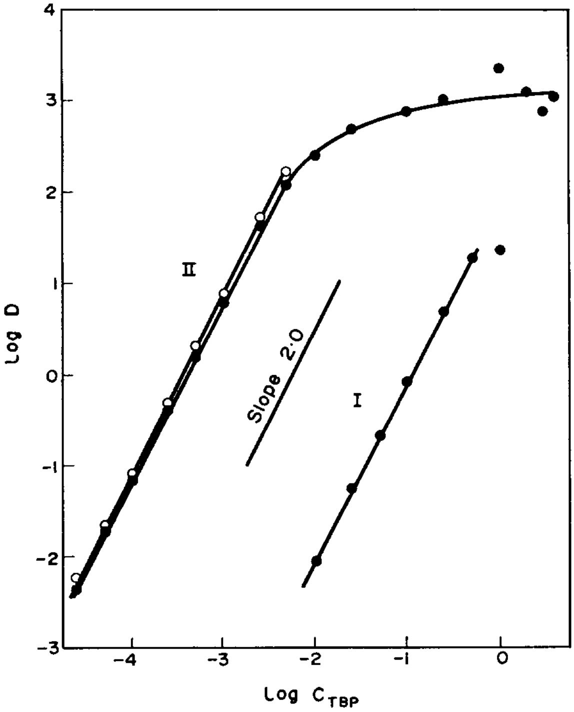


FIG. 1.—Distribution ratio of hafnium as a function of TBP concentration in benzene.
I. HCl 7.0M; Hf(IV) 5·60 × $10^{-5}M$, ● (slope 1·95)
II. HCl 10M; Hf(IV) trace, ○ (slope 2·05); 5·60 × $10^{-5}M$, ● (slope 2·0) C_{TBP} = initial TBP concentration in benzene (M)

The curves of log D *vs.* C_{acid} are similar for both MIBK and TBP with a given aqueous medium, but a much higher acidity is needed for extraction with MIBK. Hafnium is quantitatively extracted with TBP, from 7·5–11M hydrochloric acid. Hafnium was hardly extracted at all from sulphuric acid in the concentration range tested, both with MIBK and TBP, because it forms a stable anionic sulphato complex[20] and does not easily form an association compound.

A more detailed examination was made of the HCl–TBP system because of the good extraction of hafnium.

Hafnium concentration. Plots of log D *vs.* log C_{Hf} at different concentrations (5–8M) of hydrochloric acid gave straight lines with zero slope.

Chloride ion and hydrogen ion concentration. Plots of log D *vs.* log C_{Cl^-} for constant hydrogen ion concentration and constant ionic strength gave straight lines, with a slope of about 2.

Plots of log D *vs.* log C_{H^+} at constant chloride ion concentration and constant ionic strength were not linear (as shown in Fig. 2) which is the same tendency as in the case[21] of zirconium extraction from hydrochloric acid with TBP–benzene.

Stripping. After extraction of hafnium from 10M hydrochloric acid with 1M TBP in benzene, the organic phase was shaken with 10 ml of hydrochloric acid (of various concentrations) for 30 min. It was found that 1–3M hydrochloric acid quantitatively strips hafnium into the aqueous phase.

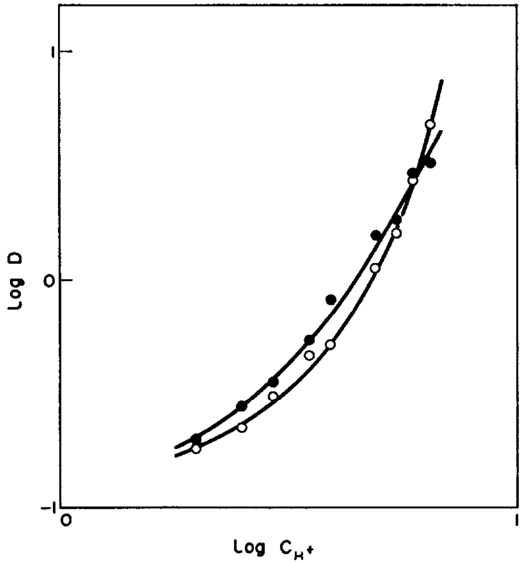


FIG. 2.—Distribution ratio of hafnium as a function of hydrogen ion concentration in the aqueous phase.

Chloride ion 6·5*M*; ionic strength 6·5; Hf(IV): trace ○, 5·60 × $10^{-5}M$ ●; TBP 1*M* in benzene; C_{H^+} = equilibrium aqueous hydrogen ion concentration (*M*).

Conclusion

When MIBK is used as the extraction solvent, good extraction of hafnium is not obtained from any kind of acid solution, but hafnium ($<5{\cdot}60 \times 10^{-4}M$) is extracted quantitatively from >7·5*M* hydrochloric acid with 1*M* TBP in benzene. Stripping with 1–3*M* hydrochloric acid gives a recovery of over 99%.

The slopes of the plots of log *D vs.* log C_{TBP} and of log *D vs.* log C_{Cl^-} are both about 2, and it may be concluded that this is the molar ratio of TBP or chlorine to hafnium in the extractable species, provided that there is no gross non-linearity of the activity of TBP or chloride ion over the concentration range examined. In contrast, the slope in the plots of log *D vs.* log C_{H^+} changes with increase in C_{H+} which can be interpreted as signifying the presence of different kinds of extractable species.

Acknowledgements—The author expresses his deep gratitude to Prof. Hidehiro Gotô of Tohoku University, Prof. Taitiro Fujinaga of Kyoto University and Rioji Takeno of Ubekosan Co. Ltd., for their kind and unfailing guidance throughout the present work.

NORIO ICHINOSE

Department of Chemistry
Faculty of Liberal Arts
Yamaguchi University
Yamaguchi, Japan

Summary—The effect of various factors on the distribution of hafnium ($<5{\cdot}60 \times 10^{-4}M$) between different acids and methyl isobutyl ketone (MIBK) or tributyl phosphate (TBP) was studied by using $^{175+181}$Hf as a tracer. When the extraction is made from 7·5–11*M* hydrochloric acid with an equal volume of 1*M* TBP in benzene, hafnium is extracted quantitatively (>99%). The hafnium can be stripped with 1–3*M* hydrochloric acid.

Zusammenfassung—Der Einfluß verschiedener Parameter auf die Verteilung von Hafnium ($<5{,}6 \cdot 10^{-4}$M) zwischen verschiedenen Säuren und Methylisobutylketon (MIBK) oder Tributylphosphat (TBP) wurde mit Hilfe von $^{175+181}$Hf als Tracer untersucht. Extrahiert man aus 7,5–11 M Salzsäure mit einem gleichen Volumen 1 M TBP in Benzol, so wird Hafnium quantitativ extrahiert (>99%). Das Hafnium kann mit 1–3 M Salzsäure rückextrahiert werden.

Résumé—On a étudié l'influence de divers facteurs sur le partage du hafnium ($\leqslant 5{,}60 \times 10^{-4}M$) entre différents acides et la méthylisobutylcétone (MIBK) ou le tributyl phosphate (TBP) en utilisant $^{175+181}$Hf comme traceur. Lorsque l'extraction est faite à partir d'acide chlorhydrique 7,5–11M avec un égal volume de TBP 1M en benzène, le hafnium est extrait quantitativement (>99%). Le hafnium peut être extrait à l'acide chlorhydrique 1–3M.

REFERENCES

1. R. A. Foos and H. A. Wilhelm, *U.S. At. Energy Comm. Rept.*, ISC-693, 1959, 38.
2. F. Fudswell, J. C. H. Waldron and B. R. Harder, *At. Energy Research Estab.* (*Gt. Brit.*) C/R 1520, 1956, 7.
3. H. A. Wilhelm, K. A. Walsh and J. V. Kerrigan, *U.S. Patent* 2,753,250, July 3, 1956.
4. R. P. Cox, *Iowa State Coll. J. Sci.*, 1957, **31**, 383.
5. N. Isaac and R. de Witte, *Energie Nucleaire*, 1957, **1**, 71.
6. R. P. Cox, H. C. Peterson and G. H. Beyer, *Ind. Eng. Chem.*, 1958, **50**, 141.
7. F. R. Sánchez, F. d. l. C. Castillo and R. F. Cellini, *Anales Real Soc. Espan. Fis. y Quim.* (*Madrid*), 1960, **56B**, 869.
8. G. F. Egorov, V. V. Fomin, Y. G. Frolov and G. A. Yagadin, *Zh. Neorgan. Khim.*, 1960, **5**, 1044.
9. J. Huré, M. Rastoix and R. S. James, *Anal. Chim. Acta*, 1961, **25**, 1.
10. *Idem, ibid.*, 1961, **25**, 118.
11. T. Patzek, *Prace Inst. Hutniczvch*, 1961, **13**, 73.
12. A. M. Reznik, A. M. Rozen, S. S. Korovin and I. A. Apraksin, *Dokl. Akad. Nauk SSSR*, 1962, **143**, 1413.
13. V. Yatirajam, *J. Sci. Ind. Res.* (*India*), 1962, **21D**, 196.
14. L. N. Komissarova, Y. V. Granovskii, N. M. Prutkova, Y. P. Adler, V. V. Nalimov and V. I. Spitsyn, *Zavodsk. Lab.*, 1963, **29**, 65.
15. A. M. Reznik, A. M. Rozen, S. S. Korovin and I. A. Apraskin, *Radiokhimiya*, 1963, **5**, 49.
16. V. I. Spitsyn, Y. V. Granovskii and L. N. Komisarova, *Dokl. Vses. Soveshch. Plan. Eksp.*, *1st, Moscow*, 1964, 276.
17. I. A. Apraksin, Y. M. Gluboko, S. S. Korovin and A. M. Reznik, *Zh. Neorgan. Khim.*, 1964, **9**, 2023.
18. S. S. Korovin, E. N. Lebedeva, A. M. Rozen, A. M. Reznik, A. V. Makeshina and V. N. Solomakhina, *ibid.*, 1969, **12**, 1006.
19. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., p. 725. Macmillan, London, 1952.
20. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, p. 419. Pergamon, Oxford, 1969.
21. A. E. Levitt and H. Freund, *J. Am. Chem. Soc.*, 1956, **78**, 1545.

Talanta, 1972, Vol. 19, pp. 1647 to 1650. Pergamon Press. Printed in Northern Ireland

Non-destructive method for the analysis of gold(I) cyanide plating baths
Complexometric determination of nickel and indium

(*Received* 24 *June* 1971, *Accepted* 25 *March* 1972)

PURE GOLD, although chemically inactive, is not mechanically resistant in thin coatings and not suitable, for example, for printed circuits that are subject to high mechanical stress. Therefore various electrolytically plated gold alloys have been proposed for electronic purposes. The quality of the coatings is of course dependent on the composition of the gold baths. Besides the main component [potassium cyanoaurate(I)] other metals such as indium, nickel, cobalt are used, mostly as citrate complexes. Regular control of such baths is desirable. Gravimetric methods are tedious and require the total destruction of organic matter. Among volumetric methods only EDTA titrations

man aus 7,5–11 M Salzsäure mit einem gleichen Volumen 1 M TBP in Benzol, so wird Hafnium quantitativ extrahiert (>99%). Das Hafnium kann mit 1–3 M Salzsäure rückextrahiert werden.

Résumé—On a étudié l'influence de divers facteurs sur le partage du hafnium ($\leqslant 5,60 \times 10^{-4}M$) entre différents acides et la méthylisobutylcétone (MIBK) ou le tributyl phosphate (TBP) en utilisant $^{175+181}$Hf comme traceur. Lorsque l'extraction est faite à partir d'acide chlorhydrique 7,5–11*M* avec un égal volume de TBP 1*M* en benzène, le hafnium est extrait quantitativement (>99%). Le hafnium peut être extrait à l'acide chlorhydrique 1–3*M*.

REFERENCES

1. R. A. Foos and H. A. Wilhelm, *U.S. At. Energy Comm. Rept.*, ISC-693, 1959, 38.
2. F. Fudswell, J. C. H. Waldron and B. R. Harder, *At. Energy Research Estab.* (*Gt. Brit.*) C/R 1520, 1956, 7.
3. H. A. Wilhelm, K. A. Walsh and J. V. Kerrigan, *U.S. Patent* 2,753,250, July 3, 1956.
4. R. P. Cox, *Iowa State Coll. J. Sci.*, 1957, **31**, 383.
5. N. Isaac and R. de Witte, *Energie Nucleaire*, 1957, **1**, 71.
6. R. P. Cox, H. C. Peterson and G. H. Beyer, *Ind. Eng. Chem.*, 1958, **50**, 141.
7. F. R. Sánchez, F. d. l. C. Castillo and R. F. Cellini, *Anales Real Soc. Espan. Fis. y Quim.* (*Madrid*), 1960, **56B**, 869.
8. G. F. Egorov, V. V. Fomin, Y. G. Frolov and G. A. Yagadin, *Zh. Neorgan. Khim.*, 1960, **5**, 1044.
9. J. Huré, M. Rastoix and R. S. James, *Anal. Chim. Acta*, 1961, **25**, 1.
10. *Idem, ibid.*, 1961, **25**, 118.
11. T. Patzek, *Prace Inst. Hutniczvch*, 1961, **13**, 73.
12. A. M. Reznik, A. M. Rozen, S. S. Korovin and I. A. Apraksin, *Dokl. Akad. Nauk SSSR*, 1962, **143**, 1413.
13. V. Yatirajam, *J. Sci. Ind. Res.* (*India*), 1962, **21D**, 196.
14. L. N. Komissarova, Y. V. Granovskii, N. M. Prutkova, Y. P. Adler, V. V. Nalimov and V. I. Spitsyn, *Zavodsk. Lab.*, 1963, **29**, 65.
15. A. M. Reznik, A. M. Rozen, S. S. Korovin and I. A. Apraskin, *Radiokhimiya*, 1963, **5**, 49.
16. V. I. Spitsyn, Y. V. Granovskii and L. N. Komisarova, *Dokl. Vses. Soveshch. Plan. Eksp.*, *1st, Moscow*, 1964, 276.
17. I. A. Apraksin, Y. M. Gluboko, S. S. Korovin and A. M. Reznik, *Zh. Neorgan. Khim.*, 1964, **9**, 2023.
18. S. S. Korovin, E. N. Lebedeva, A. M. Rozen, A. M. Reznik, A. V. Makeshina and V. N. Solomakhina, *ibid.*, 1969, **12**, 1006.
19. I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., p. 725. Macmillan, London, 1952.
20. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, p. 419. Pergamon, Oxford, 1969.
21. A. E. Levitt and H. Freund, *J. Am. Chem. Soc.*, 1956, **78**, 1545.

Talanta, 1972, Vol. 19, pp. 1647 to 1650. Pergamon Press. Printed in Northern Ireland

Non-destructive method for the analysis of gold(I) cyanide plating baths
Complexometric determination of nickel and indium

(*Received* 24 *June* 1971, *Accepted* 25 *March* 1972)

Pure gold, although chemically inactive, is not mechanically resistant in thin coatings and not suitable, for example, for printed circuits that are subject to high mechanical stress. Therefore various electrolytically plated gold alloys have been proposed for electronic purposes. The quality of the coatings is of course dependent on the composition of the gold baths. Besides the main component [potassium cyanoaurate(I)] other metals such as indium, nickel, cobalt are used, mostly as citrate complexes. Regular control of such baths is desirable. Gravimetric methods are tedious and require the total destruction of organic matter. Among volumetric methods only EDTA titrations can be considered, but the presence of citrate and citric acid (up to 100 g/l.) makes complexometric determination impossible. In addition the baths contain incidental impurities such as iron and copper. Gold ions also interfere with the colour changes of indicators.

Complexometric determination of indium, nickel, zinc, and aluminium after decomposition of gold baths with sulphuric and nitric acids was described by the present authors some years ago.[1] No attempts have been made to determine the alloying metals without time-consuming destruction of the organic acid present in the baths. The method described below makes it possible to determine indium and nickel within 40 min. It is based on the following principle.

Gold(I) cyanide is extracted from the acidic solution with ethyl acetate. The extract can be used for recovery of the gold in the usual way. After the gold extraction a suitable aliquot is used for the separation of nickel. Indium is masked with thioglycollic acid and nickel precipitated with sodium diethyldithiocarbamate and extracted with chloroform. Nickel is then stripped from the organic phase with mercuric chloride and determined complexometrically. In another aliquot indium and nickel are precipitated with the same reagent (without addition of thioglycollic acid), extracted into chloroform, and stripped with mercuric chloride. Nickel is masked with 1,10-phenanthroline and indium titrated directly with EDTA.

EXPERIMENTAL

Reagents

EDTA solution, 0·02*M*. Standardized with 0·02*M* zinc chloride or lead nitrate (Xylenol Orange as indicator).

Indium chloride solution, 0·01*M*. Prepared by dissolution of 2·2964 g of metallic indium in 25 ml of hydrochloric acid (1 + 1) and dilution to 1 litre.

Nickel nitrate solution, 0·01*M*. Prepared by dissolution of 2·95 g of the hexahydrate in 1 litre of redistilled water.

1,10-*Phenanthroline solution*, 0·1*M*. Prepared by suspending 18·02 g of reagent in 50 ml of water and adding 1*M* hydrochloric acid dropwise till all is dissolved, then diluting to 100 ml.

Saturated mercuric chloride solution.

Buffer solution, pH 3. Monochloroacetic solution (0·2*M*) neutralized with 1*M* sodium hydroxide to the desired pH.

Thioglycollic acid solution. Prepared by diluting 20 ml of the 80% acid solution to 100 ml with water.

Other reagents include 0·5% aqueous Xylenol Orange solution, 10% potassium chloride solution, potassium iodide solution, solid hexamine, thiourea, and 0·15*M* sodium diethyldithiocarbamate (3·4 g of reagent in 100 ml of water, prepared fresh daily).

Procedure

Separation of gold. Transfer by pipette a sample of gold-bath solution containing not more than 25 mg of indium and 15 mg of nickel, into a 150–250 ml separatory funnel, adjust the acidity to 0·2–0·3*N* with 1*M* hydrochloric acid, add 5 ml of 10% potassium chloride solution and extract twice with 20-ml portions of ethyl acetate. Separate the phases, remove the organic layer and transfer the aqueous solution into a 25- or 50-ml standard flask.

Determination of nickel. To an aliquot of the gold-free solution containing up to 6 mg of nickel add 5 ml of 10% potassium chloride solution, 1–2 ml of thioglycollic acid solution and make alkaline by addition of 5 ml of 5% ammonia solution. (The solution must be alkaline before the precipitation of nickel, otherwise indium is not quantitatively masked.) Now add 3–4 ml of 0·15*M* sodium diethyldithiocarbamate to precipitate nickel. Adjust the volume to about 30 ml and extract twice with 20 ml of chloroform. Collect both extracts in another separatory funnel, add 10 ml of 0·2*M* hydrochloric acid, and 5 ml of potassium chloride solution. The solution must be acid (pH control). Then add 4–5 ml of saturated mercuric chloride solution and shake for 2 min. The quantitative stripping of nickel is indicated by disappearance of the green colour of the organic phase. Separate the aqueous layer into a 400-ml titration flask, wash the organic layer with water containing a little potassium chloride solution and add the washings to the titration flask. Add 5% potassium iodide solution until the yellow precipitate dissolves (masking of excess of mercuric chloride. Add 10 ml of 0·02*M* EDTA, dilute, and adjust the pH to 5–5·5 with 0·2*M* hydrochloric acid and solid hexamine. Add a few drops of Xylenol Orange indicator and titrate slowly with 0·02*M* zinc chloride to the end-point indicated by a colour change from lemon yellow to red-violet.

During the titration the solution usually become cloudy but this does not affect the end-point. Mercury together with copper can also be masked with thiourea.

(1 ml of 0·02*M* EDTA corresponds to 1·174 mg of Ni.)

Determination of indium. To an aliquot containing up to 10 mg of indium and 6 mg of nickel add 10 ml of 0·2*M* hydrochloric acid, 5 ml of 10% potassium chloride solution and 3–4 ml of 0·15*M* sodium diethyldithiocarbamate. Continue as described for nickel.

After stripping indium and nickel with mercuric chloride add 0·5 g of thiourea to mask excess of mercury, then 20 ml of monochloroacetic acid buffer and 3 ml of 0·1*M* 1,10-phenanthroline to mask nickel. At this stage the pH must be 3. Dilute to 100–120 ml, warm to 70–80°, add Xylenol Orange indicator and titrate slowly with 0·02*M* EDTA to the end-point indicated by a colour change from violet to lemon yellow.

(1 ml of 0·02*M* EDTA corresponds to 2·736 mg of In.)

Typical results are given in Table I.

TABLE I.—DETERMINATION OF NICKEL AND INDIUM IN THE PRESENCE OF 400–500 mg OF CITRIC ACID

Taken, *mg*		Found, *mg*	Taken, *mg*		Found, *mg*
In	Ni	Ni	In	Ni	In
5·70	3·03	2·80	1·14	0·60	1·07
2·27	1·51	1·53	1·14	4·55	1·18
11·41	0·76	0·76	2·27	4·55	2·25
1·14	6·06*	6·05	5·70	3·03	5·61
1·42	12·12†	12·24	5·70	4·55	5·61
9·12	4·85	4·84			
3·44	0·31	0·23			

* Small precipitate between the two phases.

† Poor separation. The organic layer had to be washed with potassium chloride solution.

Remarks

Copper does not interfere. It is precipitated and extracted together with nickel and indium and also stripped into the aqueous phase but it is masked before titration, either with thiourea or 1,10-phenanthroline.

The procedure can be modified as follows. In one aliquot indium and nickel are precipitated with sodium diethyldithiocarbamate and extracted. Their sum is determined by indirect titration with EDTA after stripping with mercuric chloride.

In another aliquot, nickel is determined as already described. This method has the advantage that the relatively expensive 1,10-phenanthroline is not needed.

Practical application

The procedure was tested by analysis of the gold-baths used at the Establishment for Industrial Automation in Nová Paka. The gravimetric results for indium and nickel after the destruction of organic matter gave on average 3·89 mg/ml for indium and 0·76 mg/ml for nickel. Our results by the extraction method were 3·61 and 3·73 mg/ml for indium and 0·71 and 0·69 mg/ml for nickel.

Acknowledgement—The authors are grateful to Dr. B. Rejha (Establishment for Industrial Automation) for providing the samples of gold-baths, and for his keen interest in their work.

Laboratory of Analytical Chemistry
J. Heyrovský Polarographic Institute
Czechoslovak Academy of Sciences
Prague 1, *Jilská* 16 *Czechoslovakia*

RUDOLF PŘIBIL
VLADIMÍR VESELÝ

Summary—A method is described for rapid determination of nickel and indium in gold(I) cyanide baths containing large amounts of citric acid and/or sodium citrate, without previous destruction of organic matter. Gold is removed by extraction with ethyl acetate. In one aliquot of the solution indium is masked with thioglycollic acid and nickel is precipitated with sodium diethyldithiocarbamate, extracted into chloroform, stripped into water and determined complexometrically.

In a second aliquot indium and nickel are precipitated together with the same reagent and stripped into water, then nickel is masked with 1,10-phenanthroline, and indium is determined by direct titration with EDTA.

Zusammenfassung—Zur raschen Bestimmung von Nickel und Indium in Gold(I)-cyanidbädern, die große Mengen Zitronensäure und/oder Natriumcitrat enthalten, wird ein Verfahren beschrieben, das ohne die vorhergehende Zerstörung des organischen Materials auskommt. Gold wird durch Extraktion mit Äthylacetat entfernt. In einem aliquoten Teil der Lösung wird Indium mit Thioglykolsäure maskiert und Nickel mit Natriumdiäthyldithiocarbamat gefällt, in Chloroform extrahiert, in Wasser rückextrahiert und komplexometrisch bestimmt. In einem zweiten aliquoten Teil werden Indium und Nickel zusammen mit dem selben Reagens gefällt, die Komplexe in Wasser wieder zerlegt, Nickel mit 1,10-Phenanthrolin maskiert und Indium durch direkte Titration mit EDTA bestimmt.

Résumé—On décrit une méthode pour le dosage rapide du nickel et de l'indium dans des bains de cyanure d'or(I) contenant de grandes quantités d'acide citrique et/ou de citrate de sodium, sans destruction préalable de la matière organique. On élimine l'or par extraction à l'acétate d'éthyle. Dans une partie aliquote de la solution, on dissimule l'indium par l'acide thioglycolique, et le nickel est précipité par le diéthyldithiocarbamate de sodium, extrait en chloroforme, réextrait dans l'eau et dosé complexométriquement. Dans une seconde partie aliquote, l'indium et le nickel sont précipités ensemble par le même réactif et redissous dans l'eau, puis le nickel est dissimulé par la 1,10-phénanthroline, et l'on dose l'indium par titrage direct à l'EDTA.

REFERENCE

1. R. Přibil and V. Veselý, *Chemist-Analyst*, 1966, **55**, 38.

Talanta, 1972, Vol. 19, pp. 1650 to 1654. Pergamon Press. Printed in Northern Ireland

Potentiometric argentimetric method for the successive titration of sulphide and dissolved sulphur in polysulphide solutions

(*Received* 26 *July* 1971. *Accepted* 30 *March* 1972)

AS IS COMMONLY KNOWN, free sulphur dissolves in an alkaline solution of sulphide to form polysulphides.

$$S^{2-} + (x - 1)S = S_x^{2-}$$

We denote one sulphur atom in each polysulphide ion as sulphide sulphur (S^{2-}), and the rest of the ion (S_{x-1}) as dissolved sulphur.

Various methods to determine polysulphide have already been presented.[1-14] Most of these, however, are rather complicated and time-consuming. For the simultaneous determination of S^{2-} and S_{x-1}, Papp and Havas[13] have recently developed a potentiometric method using mercuric chloride as the titrant and a sulphide-ion selective electrode as the indicator. This method is useful, particularly for the routine analysis of kraft cooking and waste liquors, which contain reducing organic substances and others, in sulphate pulping processes. It seems, however, that argentimetry is also worth further study for the simple and accurate analysis of polysulphide solutions that contain no reducing substances, and this is one of the purposes of our present study.

Ikeda and Musha[8] previously reported that S_{x-1} in polysulphide solutions can be determined rapidly and accurately by means of a short-circuit amperometric titration with silver nitrate. The replacement of the amperometric means of end-point detection in this procedure by such potentiometric means as a sulphide-ion selective electrode permits successive determination of S^{2-} and S_{x-1}. The

In a second aliquot indium and nickel are precipitated together with the same reagent and stripped into water, then nickel is masked with 1,10-phenanthroline, and indium is determined by direct titration with EDTA.

Zusammenfassung—Zur raschen Bestimmung von Nickel und Indium in Gold(I)-cyanidbädern, die große Mengen Zitronensäure und/oder Natriumcitrat enthalten, wird ein Verfahren beschrieben, das ohne die vorhergehende Zerstörung des organischen Materials auskommt. Gold wird durch Extraktion mit Äthylacetat entfernt. In einem aliquoten Teil der Lösung wird Indium mit Thioglykolsäure maskiert und Nickel mit Natriumdiäthyldithiocarbamat gefällt, in Chloroform extrahiert, in Wasser rückextrahiert und komplexometrisch bestimmt. In einem zweiten aliquoten Teil werden Indium und Nickel zusammen mit dem selben Reagens gefällt, die Komplexe in Wasser wieder zerlegt, Nickel mit 1,10-Phenanthrolin maskiert und Indium durch direkte Titration mit EDTA bestimmt.

Résumé—On décrit une méthode pour le dosage rapide du nickel et de l'indium dans des bains de cyanure d'or(I) contenant de grandes quantités d'acide citrique et/ou de citrate de sodium, sans destruction préalable de la matière organique. On élimine l'or par extraction à l'acétate d'éthyle. Dans une partie aliquote de la solution, on dissimule l'indium par l'acide thioglycolique, et le nickel est précipité par le diéthyldithiocarbamate de sodium, extrait en chloroforme, réextrait dans l'eau et dosé complexométriquement. Dans une seconde partie aliquote, l'indium et le nickel sont précipités ensemble par le même réactif et redissous dans l'eau, puis le nickel est dissimulé par la 1,10-phénanthroline, et l'on dose l'indium par titrage direct à l'EDTA.

REFERENCE

1. R. Přibil and V. Veselý, *Chemist-Analyst*, 1966, **55**, 38.

Talanta, 1972, Vol. 19, pp. 1650 to 1654. Pergamon Press. Printed in Northern Ireland

Potentiometric argentimetric method for the successive titration of sulphide and dissolved sulphur in polysulphide solutions

(*Received* 26 *July* 1971. *Accepted* 30 *March* 1972)

As is commonly known, free sulphur dissolves in an alkaline solution of sulphide to form polysulphides.

$$S^{2-} + (x - 1)S = S_x^{2-}$$

We denote one sulphur atom in each polysulphide ion as sulphide sulphur (S^{2-}), and the rest of the ion (S_{x-1}) as dissolved sulphur.

Various methods to determine polysulphide have already been presented.[1-14] Most of these, however, are rather complicated and time-consuming. For the simultaneous determination of S^{2-} and S_{x-1}, Papp and Havas[13] have recently developed a potentiometric method using mercuric chloride as the titrant and a sulphide-ion selective electrode as the indicator. This method is useful, particularly for the routine analysis of kraft cooking and waste liquors, which contain reducing organic substances and others, in sulphate pulping processes. It seems, however, that argentimetry is also worth further study for the simple and accurate analysis of polysulphide solutions that contain no reducing substances, and this is one of the purposes of our present study.

Ikeda and Musha[8] previously reported that S_{x-1} in polysulphide solutions can be determined rapidly and accurately by means of a short-circuit amperometric titration with silver nitrate. The replacement of the amperometric means of end-point detection in this procedure by such potentiometric means as a sulphide-ion selective electrode permits successive determination of S^{2-} and S_{x-1}. The advantage of the proposed method is that the content of these two species can be calculated directly from the two titration steps for the same sample. In this method, polysulphide solutions are titrated by silver nitrate after the cyanolysis of polysulphide ions and the subsequent masking of the excess of cyanide ions with formaldehyde.

$$S_x^{2-} + (x - 1)CN^- = S^{2-} + (x - 1)SCN^-$$

EXPERIMENTAL

Materials and apparatus

All the chemicals used were of reagent grade.

Polysulphide stock solution. Dissolve about 12 g of crystalline sodium sulphide and about 1·6 g of powdered sulphur in 30 ml of oxygen-free water in a 100-ml flask with the aid of shaking for about 1 hr at room temperature. Dilute the solution to 100 ml to give a 0·05*M* sodium polysulphide stock solution, the colour of which is reddish brown. The surface of the solution is covered with liquid paraffin to prevent aerial oxidation. Working solutions are prepared by further dilution.

Automatic recording potentiometric titrator. A Hiranuma RAT-101 instrument with a sulphide ion selective electrode (Orion, Model 94-16) and a saturated calomel electrode was used.

Procedure

Place a definite amount of the stock solution in a titration cell under an atmosphere of nitrogen, and cover the surface of the solution with a 1-cm thick liquid paraffin layer. Add an excess of potassium cyanide solution, which should be gently poured against the wall of the cell so that air bubbles are not entrained. Heat the solution to 40–50° until its reddish brown (or yellow) colour disappears (10 min), and then allow it to stand for 2 min. Cool the solution to below 15°, and add 2 or 3 drops of phenolphthalein indicator. Add sufficient formaldehyde and adjust the pH of the solution to 3 with dilute sulphuric acid (in order to mask the residual cyanide ions) then, without delay, make the solution alkaline again (pale pink) with dilute ammonia water, and finally add oxygen-free water to make up to about 100 ml. Titrate this solution with a standardized silver nitrate solution until the titration curve shows a sudden change, which corresponds to the first end-point (Fig. 1). Then adjust the pH of the solution to below 3 with dilute sulphuric acid, and continue the titration until the second end-point is reached. The first is for sulphide ion (free sulphide plus the sulphide bound by polysulphide), and the second for thiocyanate ion (consequently, for dissolved sulphur originally present).

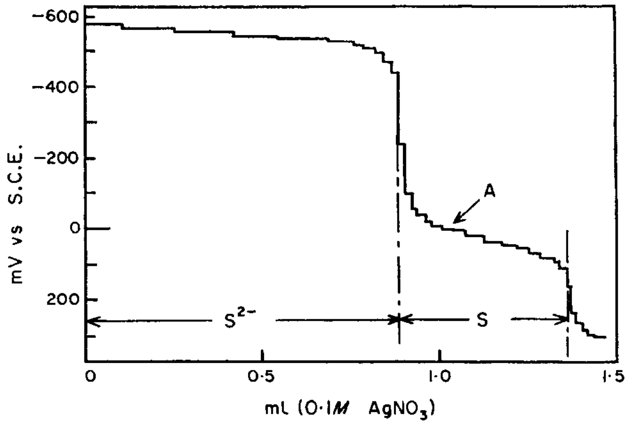


FIG. 1.—Titration curve for 100 ml of 5 × $10^{-4}M$ polysulphide solution containing 1·6 mg of S.
(A) Around here, 1*M* H_2SO_4 was added.

In the case of concentrated samples, if precipitates settle to the electrode they may reduce its response, so the cell must be occasionally shaken during titration.

RESULTS AND DISCUSSION

The present method was compared with two others, the iodometric method reported by Szekeres[4] and the amperometric method by Ikeda and Musha;[8] the results are listed in Tables I and II. Table I shows the analytical values obtained for each 100-ml volume of a $5 \times 10^{-3}M$ polysulphide solution, originally containing about 16 mg of dissolved sulphur. The values obtained by the proposed method are in good agreement with those obtained by the other two, which shows the proposed method is as good as the established methods. Table II shows the results for solutions of various concentrations and compositions. It indicates that the proposed method is capable of determining 5×10^{-5}–$5 \times 10^{-3}M$ S^{2-} and 0·16–20 mg of sulphur with good accuracy and reproducibility.

Further, the method was compared (for higher polysulphides) with the mercurimetric method of Papp and Havas.[13] The results are listed in Table III. Calculated values of x in S_x^{2-} indicate that S_4^{2-} as well as S_2^{2-} or S_3^{2-} can be determined by our method.

TABLE I.—COMPARISON OF ANALYTICAL VALUES BY THREE METHODS

	S^{2-}			S		
	This method	Iodometry	Difference	This method	Amperometry	Difference
Found, *mg*	14·38	14·34	0·04	15·89	15·83	0·06
Coefficient of variation, %	0·05	0·07	—	0·4	0·3	—

Each value is the average of 4 titrations.

TABLE II.—ACCURACY AND REPRODUCIBILITY AT VARIOUS CONCENTRATIONS AND COMPOSITIONS

Concentration		S^{2-}		S	
S^{2-}, M	S, *mg*/100 ml	Difference*, %	Coefficient of variation %	Difference,† %	Coefficient of variation, %
5×10^{-3}	5	+0·2	0·4	−1·3	0·5
5×10^{-3}	10	+0·1	0·2	+0·3	0·4
5×10^{-3}	16	+0·2	0·1	+0·4	0·3
5×10^{-3}	20	+0·4	0·5	+0·5	0·5
5×10^{-4}	1·6	+1·0	0·3	−1·1	0·6
5×10^{-5}	0·16	+0·1	0·6	−2·5	0·8

* Difference between the value found by the proposed method and the value expected for each specified concentration of S^{2-} from the value found by iodometry for 100 ml of $5 \times 10^{-3}M$ polysulphide solution containing 16 mg of S.

† The meaning is similar to that for S^{2-}, except that the reference value for S was obtained by the amperometric method.

Each value is the average of 4 titrations.

Though the values for sulphide sulphur by the two methods agreed well, the values for dissolved sulphur by argentimetry were about 5% smaller than those by mercurimetry. The potential change at the end-point for dissolved sulphur was sharper and more stable in argentimetry than in mercurimetry. The sulphide values by our method and by Papp's always give the sum of the amounts of free and bound sulphide in polysulphide solutions.

During the analysis, hydrogen sulphide and hydrogen cyanide were not evolved from the solutions, because the cyanolysis of polysulphide was carried out in alkaline solution and the subsequent acidification of the solution was quickly done, the surface being covered with liquid paraffin. Hydrogen cyanide was, of course, not evolved after the masking of cyanide ions by formation of formaldehyde cyanhydrin in the acidic solution.

The presence of sodium hydroxide, sodium carbonate, or sodium sulphate (the concentration of each being 0·05*N*) did not disturb the proposed method. Sodium thiosulphate caused a positive error in the values found for dissolved sulphur, as was to be expected because of its cyanolysis to form thiocyanate.

SANAE IKEDA
HIROMU SATAKE
TAKEO HISANO
TOSHIO TERAZAWA

Department of Applied Chemistry
Faculty of Engineering
Tokushima University
Tokushima, Japan

Table III.—Comparison of argentimetric and mercurimetric methods

Sample No.	Analytical value (Titrant, 0·1000N)						Calcd. as S_x^{2-}	
	S^{2-}			S				
	AgNO$_3$, *ml*	HgCl$_2$, *ml*	Difference, %	AgNO$_3$, *ml*	HgCl$_2$, *ml*	Difference, %	AgNO$_3$ method	HgCl$_2$ method
1	9·71 (0·3)	9·70 (0·2)	+0·1	5·02 (0·4)	5·31 (0·7)	−5·5	$S_{2\cdot0}^{2-}$	$S_{2\cdot1}^{2-}$
2	9·85 (0·1)	9·84 (0·1)	+0·1	10·71 (0·5)	11·24 (0·7)	−4·7	$S_{3\cdot2}^{2-}$	$S_{3\cdot3}^{2-}$
3	11·70 (0·2)	11·60 (0·1)	+0·9	17·23 (0·2)	18·16 (0·4)	−5·2	$S_{4\cdot0}^{2-}$	$S_{4\cdot1}^{2-}$

( ); Coefficient of variation, %.
Each value is the average of 5 titrations (100 ml of 5 × $10^{-3}M$ S_x^{2-}).

Summary—Sulphide sulphur and dissolved sulphur in a polysulphide solution can be successively determined with satisfactory accuracy and reproducibility by potentiometric argentimetry in which a sulphide-selective indicator electrode is used. Before the titration, polysulphide ions need to be converted by an excess of potassium cyanide into thiocyanate and sulphide ions. The excess of cyanide ions is masked with formaldehyde and sulphuric acid, then the solution is made alkaline with ammonia and titrated with silver nitrate till the first end-point is reached (sulphide sulphur). After the acidification of the solution with sulphuric acid, the titration is continued till the second end-point is attained (dissolved sulphur).

Zusammenfassung—Sulfidschwefel und gelöster Schwefel in einer Polysulfidlösung können ausreichend genau und reproduzierbar durch potentiometrische Argentimetrie mit einer sulfidspezifischen Indikatorektrode bestimmt werden. Vor der Titration müssen Polysulfidionen mit einem Überschuß von Kaliumcyanid zu Thiocyanat- und Sulfidionen umgesetzt werden. Der Überschuß an Cyanidionen wird mit Formaldehyd und Schwefelsäure maskiert, dann wird die Lösung mit Ammoniak alkalisch gemacht und mit Silbernitrat bis zum ersten Endpunkt (Sulfidschwefel) titriert. Nach Ansäuern der Lösung mit Schwefelsäure wird die Titration fortgesetzt, bis man den zweiten Endpunkt erreicht (gelöster Schwefel).

Résumé—Le soufre à l'état de sulfure et le soufre dissous dans une solution de polysulfure peuvent être déterminés successivement avec une précision et une reproductibilité satisfaisantes par une argentimétrie potentiométrique dans laquelle on utilise une électrode indicatrice sélective des sulfures. Avant le titrage, les ions polysulfure doivent être convertis par un excès de cyanure de potassium en ions thiocyanate et sulfure. L'excès d'ions cyanure est dissimulé par le formaldéhyde et l'acide sulfurique, puis la solution est alcalinisée par l'ammoniaque et titrée par le nitrate d'argent jusqu'à ce que le premier point de fin de dosage soit atteint (soufre à l'état de sulfure). Après acidification de la solution par l'acide sulfurique, on poursuit le titrage jusqu'à ce que le second point de fin de dosage soit atteint (soufre dissous).

REFERENCES

1. H. A. J. Pieters, and C. Popelier, *Chem. Zentr.*, 1943, **1**, 1393.
2. F. Fehér and H. J. Berthold, *Z. Anal. Chem.*, 1953, **138**, 245.
3. L. Szekeres, *Acta Chim. Acad. Sci Hung.*, 1961, **26**, 167; *Chem. Abstr.*, 1961, **55**, 23184.
4. L. Légrádi, *Analyst*, 1961, **86**, 854.
5. E. Schulek, *Z. Anal. Chem.*, 1925, **65**, 352; I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, p. 307. Interscience, New York, 1957.
6. L. Szekeres, *Pharm. Zentralhalle*, 1963, **102**, 6; *Chem. Abstr.*, 1963, **58**, 13134.
7. J. E. Olsson and O. Samuelson, *Svensk Papperstid.*, 1965, **68**, 179; *Chem. Abstr.*, 1965, **63**, 3158.
8. S. Ikeda and S. Musha, *Kogyo Kagaku Zasshi*, 1970, **73**, 296.
9. A. Teder, *Svensk Papperstid.*, 1967, **70**, 197.
10. K. Johnsen, *Norsk Skogindustri*, 1966, **20**, 91.
11. E. Bilberg, *ibid.*, 1959, **13**, 307.
12. E. Bilberg and P. Landmark, *ibid.*, 1959, **13**, 375.
13. J. Papp and J. Havas, *Hung. Sci. Instr.*, 1970, **17**, 17.
14. J. Papp, *Svensk Papperstid.*, 1971, **74**, 310.

Talanta, 1972, Vol. 19, pp. 1654 to 1658. Pergamon Press. Printed in Northern Ireland

Cation-exchange of metal ions in organic solvent–cupferron media

(*Received* 13 *March* 1972. *Accepted* 1 *May* 1972)

RECENTLY, the use of common extractants, as employed in the liquid-liquid extraction of metal ions, has been studied with respect to their applicability to ion-exchange.[1–5] The strongly acidic cation-exchanger Dowex 50 has proved highly successful. On this exchanger several unique separations of

Summary—Sulphide sulphur and dissolved sulphur in a polysulphide solution can be successively determined with satisfactory accuracy and reproducibility by potentiometric argentimetry in which a sulphide-selective indicator electrode is used. Before the titration, polysulphide ions need to be converted by an excess of potassium cyanide into thiocyanate and sulphide ions. The excess of cyanide ions is masked with formaldehyde and sulphuric acid, then the solution is made alkaline with ammonia and titrated with silver nitrate till the first end-point is reached (sulphide sulphur). After the acidification of the solution with sulphuric acid, the titration is continued till the second end-point is attained (dissolved sulphur).

Zusammenfassung—Sulfidschwefel und gelöster Schwefel in einer Polysulfidlösung können ausreichend genau und reproduzierbar durch potentiometrische Argentimetrie mit einer sulfidspezifischen Indikatorektrode bestimmt werden. Vor der Titration müssen Polysulfidionen mit einem Überschuß von Kaliumcyanid zu Thiocyanat- und Sulfidionen umgesetzt werden. Der Überschuß an Cyanidionen wird mit Formaldehyd und Schwefelsäure maskiert, dann wird die Lösung mit Ammoniak alkalisch gemacht und mit Silbernitrat bis zum ersten Endpunkt (Sulfidschwefel) titriert. Nach Ansäuern der Lösung mit Schwefelsäure wird die Titration fortgesetzt, bis man den zweiten Endpunkt erreicht (gelöster Schwefel).

Résumé—Le soufre à l'état de sulfure et le soufre dissous dans une solution de polysulfure peuvent être déterminés successivement avec une précision et une reproductibilité satisfaisantes par une argentimétrie potentiométrique dans laquelle on utilise une électrode indicatrice sélective des sulfures. Avant le titrage, les ions polysulfure doivent être convertis par un excès de cyanure de potassium en ions thiocyanate et sulfure. L'excès d'ions cyanure est dissimulé par le formaldéhyde et l'acide sulfurique, puis la solution est alcalinisée par l'ammoniaque et titrée par le nitrate d'argent jusqu'à ce que le premier point de fin de dosage soit atteint (soufre à l'état de sulfure). Après acidification de la solution par l'acide sulfurique, on poursuit le titrage jusqu'à ce que le second point de fin de dosage soit atteint (soufre dissous).

REFERENCES

1. H. A. J. Pieters, and C. Popelier, *Chem. Zentr.*, 1943, **1**, 1393.
2. F. Fehér and H. J. Berthold, *Z. Anal. Chem.*, 1953, **138**, 245.
3. L. Szekeres, *Acta Chim. Acad. Sci Hung.*, 1961, **26**, 167; *Chem. Abstr.*, 1961, **55**, 23184.
4. L. Légrádi, *Analyst*, 1961, **86**, 854.
5. E. Schulek, *Z. Anal. Chem.*, 1925, **65**, 352; I. M. Kolthoff and R. Belcher, *Volumetric Analysis*, Vol. III, p. 307. Interscience, New York, 1957.
6. L. Szekeres, *Pharm. Zentralhalle*, 1963, **102**, 6; *Chem. Abstr.*, 1963, **58**, 13134.
7. J. E. Olsson and O. Samuelson, *Svensk Papperstid.*, 1965, **68**, 179; *Chem. Abstr.*, 1965, **63**, 3158.
8. S. Ikeda and S. Musha, *Kogyo Kagaku Zasshi*, 1970, **73**, 296.
9. A. Teder, *Svensk Papperstid.*, 1967, **70**, 197.
10. K. Johnsen, *Norsk Skogindustri*, 1966, **20**, 91.
11. E. Bilberg, *ibid.*, 1959, **13**, 307.
12. E. Bilberg and P. Landmark, *ibid.*, 1959, **13**, 375.
13. J. Papp and J. Havas, *Hung. Sci. Instr.*, 1970, **17**, 17.
14. J. Papp, *Svensk Papperstid.*, 1971, **74**, 310.

Talanta, 1972, Vol. 19, pp. 1654 to 1658. Pergamon Press. Printed in Northern Ireland

Cation-exchange of metal ions in organic solvent–cupferron media

(*Received* 13 *March* 1972. *Accepted* 1 *May* 1972)

Recently, the use of common extractants, as employed in the liquid-liquid extraction of metal ions, has been studied with respect to their applicability to ion-exchange.[1–5] The strongly acidic cation-exchanger Dowex 50 has proved highly successful. On this exchanger several unique separations of metal ions in organic solvent–mineral acid solutions containing certain extractants, have been found possible. The alkali metals can be selectively separated from practically all other elements on Dowex 50 by using 2-thenoyltrifluoroacetone in pyridine as eluent.[1] Another extractant that has proved to be suitable is trioctylphosphine oxide. With this extractant dissolved in tetrahydrofuran or methanol in the presence of hydrochloric or nitric acids, very effective cation-exchange separations of scandium from the rare earths,[2] of hafnium and zirconium,[3] thorium[4] or uranium[5] from a variety of elements can be achieved. With dithizone dissolved in tetrahydrofuran–nitric acid solution silver, copper, bismuth, and mercury can be separated effectively from numerous bi- and tervalent metal ions.[6]

Since cupferronates of iron, titanium, copper and other metals can be completely extracted into organic solvents such as chloroform[7,8] these systems are of potential interest for ion-exchange when making use of the principle of combined ion-exchange–solvent extraction (CIESE) described earlier.[9]

In the present paper the applicability of organic solvent–cupferron–hydrochloric acid systems for the separation of metal ions on Dowex 50 was investigated. As a result separations of several elements have found to be possible in these media.

EXPERIMENTAL

Reagents

Ion-exchange resin. Air-dried Dowex 50, X8 (100–200 mesh; hydrogen form) was used for the column and batch experiments. Before use the resin was purified as described earlier.[5]

Organic solvents. The following reagent-grade solvents were used: methanol, ethanol, diethyl ether, ethyl acetate and chloroform.

Cupferron.

Eluent solution. Freshly prepared solution of $0{\cdot}1M$ cupferron in chloroform–methanol–$1M$ hydrochloric acid (60:35:5 v/v).

Metal ions. Standard solutions of the following metal ions in $6M$ nitric acid were used: Fe(III), Cu(II), Ni(II), Zn(II), Hg(II), Co(II), Mn(II), Cd(II), Bi(III), Al(III), Ca(II), Ce(III), Ga(III), In(III), La(III), Mg(II), Sr(II), Ti(IV), Th(IV), and UO_2(II).

Determination of distribution coefficients

The batch distribution coefficients (K_d values) of the above-mentioned elements were determined as described earlier.[10] The quantitative determinations of the metal ions in the eluates and filtrates were performed by suitable methods based on EDTA titrations. Cerium was determined titrimetrically with potassium iodide and sodium thio-sulphate. Uranium was determined fluorimetrically.[11]

In the case of the solutions containing cupferron the organic matter was destroyed by successive evaporations with nitric acid (1 + 1) before the determination of the metal ion concentration.

Procedures

Pretreatment of the resin bed. Resin (1 g) is soaked for about 5 min in a few ml of the eluent solution and the slurry is transferred to the ion-exchange column (0·5 × 25 cm). The resulting resin bed is washed with 5–10 ml of the eluent solution.

Sorption and elution. Hydrochloric acid ($1M$, 0·5 ml) containing the metal ions (5 mg) to be separated, is mixed with 9·5 ml of methanol–chloroform mixture (3·5 ml of methanol and 6 ml of chloroform) containing 155 mg of cupferron. This mixture is passed through the pretreated resin bed at a flow-rate corresponding to the back-pressure of the resin column (about 0·35 ml/min). Under these conditions the ions having low K_d-values *i.e.*, Fe, Ti, Cu, Ce and Th, pass into the effluent. These elements are completely eluted by passage of about 40 ml of the eluent solution. If larger amounts of the metal ions are present, either the eluent volume or its cupferron concentration must be increased for quantitative elution.

Following the removal of cupferron and chloroform by washing the resin bed with 10–15 ml of a mixture consisting of 95% methanol and 5% $1M$ hydrochloric acid (v/v), the adsorbed elements can be eluted with 10 ml of $6M$ hydrochloric acid.

RESULTS AND DISCUSSION

Determinations of the distribution coefficients of iron, copper, zinc and nickel in organic solvent media containing 5% v/v $1M$ nitric or hydrochloric acid and which were $0{\cdot}05M$ or $0{\cdot}1M$ in cupferron gave the results listed in Tables I and II.

From these results it is seen that the presence of methanol and hydrochloric acid leads to lower K_d values of iron and copper. Also the presence of chloroform decreases the K_d values of the elements more than any other organic solvent. Further investigations were carried out with systems with higher chloroform concentrations. The most suitable system was found to be 60% chloroform–35% methanol–5% $1M$ hydrochloric acid. In this medium the K_d values of Fe, Cu and Ti are less than 10 (Table III).

Table I.—Distribution coefficients of Fe, Cu, Zn and Ni on dowex 50 in methanol and ethanol media (0·05 or 0·1M in cupferron)

System	Metal ion			
	Fe(III)	Cu(II)	Zn(II)	Ni(II)
I. 0·05M Cupferron				
95% ethanol–5% 1M HNO_3	102	670	$>3\times10^3$	$>10^3$
95% ethanol–5% 1M HCl	102	410	430	$>10^3$
95% ethanol–5% 1M HNO_3	41	410	$>10^3$	$>10^3$
95% methanol–5% 1M HCl	29	90	430	$>10^3$
II. 0·1M Cupferron				
95% ethanol–5% 1M HNO_3	83	410	$>10^3$	$>10^3$
95% ethanol–5% 1M HCl	83	240	180	$>10^3$
95% methanol–5% 1M HNO_3	41	410	$>10^3$	$>10^3$
95% methanol–5% 1M HCl	29	57	180	$>10^3$

Table II.—Distribution coefficients of Fe, Cu, Zn and Ni on dowex 50 in 50% organic solvent–45% alcohol–5% 1M HCl media (0·1M in cupferron)

System	Metal ion			
	Fe(III)	Cu(II)	Zn(II)	Ni(II)
Ethyl acetate + methanol + HCl	19	14	53	$>10^3$
Ethyl acetate + ethanol + HCl	29	38	180	$>10^3$
Diethyl ether + methanol + HCl	19	14	53	$>10^3$
Diethyl ether + ethanol + HCl	41	38	430	$>10^3$
Chloroform + methanol + HCl	3	8	40	$>10^3$

Table III.—Distribution coefficients of 20 metal ions on dowex 50 in 60% chloroform–35% methanol–5% 1M HCl in the presence and absence of 0.1M cupferron.

Metal Ion	Cupferron absent	Cupferron present
Fe(III)	5×10^2	2
Cu(II)	$>10^3$	6
Ti(IV)	4×10^2	2
Ce(III)	230	8
Th(IV)	2×10^3	9
Ga(III)	7×10^2	10
La(III)	$>10^3$	25
In(III)	$>10^4$	81
Bi(III)	230	13
Hg(II)	470	69
Ni(II)	$>10^3$	$>10^3$
Mn(II)	4×10^3	6×10^2
Cd(II)	125	8×10^3
Ca(II)	9×10^3	$>10^3$
Co(II)	4×10^3	$>10^3$
UO_2(II)	$>10^4$	9×10^3
Sr(II)	3×10^3	$>10^3$
Mg(II)	4×10^3	333
Al(III)	10^3	80
Zn(II)	10^3	40

An increase of the acidity in the mixture from 5% $1M$ to 5% 3 or $6M$ hydrochloric acid caused a decrease of the distribution coefficients of many metal ions. However, in these more acidic solutions cupferron was rapidly converted into a green compound which did not form cupferronates and hence was not effective for the elution of Fe, Cu and Ti.

To investigate the effect of cupferron on the adsorption of 20 elements on Dowex 50, their distribution coefficients were measured in the absence and presence of $0{\cdot}1M$ concentrations of the chelating agent. The results of these investigations are recorded in Table III and show that Fe, Ti, Cu, Ce and Th have low K_d-values (< 10) and hence can be readily separated from Ni, Mn, Cd, Co, Ca, U and Sr.

TABLE IV.—ELUTION CHARACTERISTICS OF Fe, Cu, Ti, Ce AND Th ON DOWEX 50

Metal ion	Breakthrough volume, *ml*	Volume of elution peak, *ml*	Elution volume, *ml*
Fe(III)	1	2	20
Cu(II)	2	6	30
Ti(IV)	1	2	30
Ce(III)	2	8	40
Th(IV)	2	9	35

In Table IV the volumes required for the complete elution of the slightly adsorbed elements are listed as well as the volumes of the eluent solution in which the concentration of the elements reaches a maximum.

Acknowledgement—Acknowledgement is made to the Austrian Ministry of Education for providing a fellowship for M. M. K.

Analytical Institute,
University of Vienna,
IX Wahringerstrasse 38,
Austria

J. KORKISCH
M. M. KHATER*

Summary—Distribution coefficients of 20 metal ions were determined on the strongly acidic cation-exchanger Dowex 50 in a 30:7:1 mixture of chloroform-methanol-$1M$ hydrochloric acid which was $0{\cdot}1M$ in cupferron. In this system the distribution coefficients of Fe(III), Ti(IV), Cu(II), Ce(III) and Th are lower by several orders of magnitude than those of Ni, Mn(II), Cd, Co(II), Ca, U(VI), and Sr. It is possible to separate these two groups of elements on an ion-exchange column.

Zusammenfassung—Verteilungskoeffizienten von 20 Metallionen wurden an dem stark sauren Kationenaustauscher Dowex 50 in einem $0{,}1M$ Cupferron enthaltenden Gemisch 30:7:1 Chloroform-Methanol-$1M$ Salzsäure bestimmt. In diesem System sind die Verteilungskoeffizienten von Fe(III), Ti(IV), Cu(II), Ce(III) und Th um mehrere Größenordnungen-kleiner als die von Ni, Mn(II), Cd, Co(II), Ca, U(VI) und Sr. Man kann diese beiden Gruppen von Elementen an einer Ionenaustauschersäule trennen.

Résumé—On a déterminé les coefficients de partage de 20 ions métalliques sur l'échangeur de cations fortement acide Dowex 50 dans un mélange 30:7:1 de chloroforme-méthanol-acide chlorhydrique $1M$ qui est $0{,}1M$ en cupferron. Dans ce système, les coefficients de partage de Fe(III), Ti(IV), Cu(II), Ce(III) et Th sont plus faibles de plusieurs orders de grandeur que ceux de Ni, Mn(II), Cd, Co(II), Ca, U(VI) et Sr. Il est possible de séparer ces deux groupes d'éléments sur une colonne échangeuse d'ions.

REFERENCES

1. J. Korkisch and K. A. Orlandini, *Anal. Chem.*, 1968, **40**, 1127.
2. K. A. Orlandini and J. Korkisch, *Separation Sci.*, 1968, **3**, 255.

---

* Present address: Cairo University, Faculty of Science, Chemistry Department, U.A.R.

3. J. Korkisch and K. A. Orlandini, *Talanta*, 1969, **16**, 45,
4. *Idem*, *Anal. Chem.*, 1952, **40**, 1952.
5. M. M. Khater and J. Korkisch, *Talanta*, 1971, **18**, 1001.
6. K. A. Orlandini and J. Korkisch, *Anal. Chim. Acta*, 1968, **43**, 459.
7. N. B. Furman, W. B. Mason and S. S. Pekola, *Anal. Chem.*, 1949, **21**, 1325.
8. G. K. Schweitzer and A. D. Norton, *Anal. Chim. Acta*, 1964, **30**, 119.
9. J. Korkisch, *Separation Sci.*, 1966, **1**, 159.
10. J. Korkisch and S. S. Ahluwalia, *Anal. Chem.*, 1966, **38**, 497.
11. T. Schönfeld, M. El Garhi, C. Friedmann and J. Veselsky, *Mikrochim. Acta*, 1960, 883.

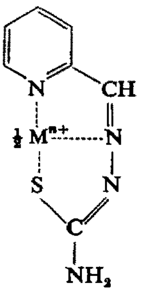
Talanta, 1972, Vol. 19, pp. 1659 to 1663. Pergamon Press. Printed in Northern Ireland

ANALYTICAL DATA

Comparative study of analytical properties and applications of picolinaldehyde thiosemicarbazone and selenosemicarbazone

(*Received* 8 *March* 1972. *Accepted* 24 *May* 1972)

Picolinaldehyde thiosemicarbazone (PAT) has been used in the photometric determination of Co(II),[1] Fe(II) and Fe(III),[2] Ni and Cu(II),[3] and their mixtures.[4] The complexes of Ni, Co(III) and Fe(II) have been isolated and studied.[5] With these cations, PAT acts as a terdentate chelating agent, and forms octahedral complexes of the type.



In certain conditions it may act as a bidentate chelating agent.

In this paper, a comparative study is made of the physical properties and chemical reactions of PAT and picolinaldehyde selenosemicarbazone (PASE), and the effect of increasing the separation of the thiosemicarbazide grouping from the pyridine ring has also been investigated, with nicotinaldehyde thiosemicarbazone (NAT). Benzaldehyde thiosemicarbazone (BAT) was also tested for comparison.

EXPERIMENTAL

Reagents

Standardized solutions of Fe(II) and Fe(III) (both 0·990 g/l.), Ni (0·986 g/l.), Co(II) (1·089 g/l.) and Cu(II) (1·995 g/l.) were used. More dilute solutions were prepared from these.

All solvents and reagents were of analytical grade.

Preparation of the compounds

PAT. A mixture of 200 ml of 0·5% aqueous thiosemicarbazide solution and 10 ml of 10% ethanolic picolinaldehyde solution was refluxed, then cooled to yield PAT, which was recrystallized from ethanol (m.p. 198–200°; found: C 46.7%; H 4.4%; N 30.9%; S 17.7%; calculated for $C_7H_8N_4S$: C 46·67%; H 4·44%; N 31·11%; S 17·72%).

BAT. Prepared similarly to PAT. White crystals, extremely bitter taste (m.p. 158–160°; found: C 53.7%; H 5.1%; N 23.7%; S 17.6%: calculated for $C_8H_9N_3S$: C 53.65%; H 5.04%; N 23.45%; S 17·88%).

PASE. Hydrazine hydrate (10·5 g) was added to 27 g of previously synthesized potassium selenocyanate dissolved in the minimum amount of water. The mixture was acidified with 3·8*M* hydrochloric acid to pH 5; 15 ml of acetone were then added, and the solution was refluxed for 90 min, cooled and filtered. The acetone selenosemicarbazone crystallized slowly in white crystals, which easily became red. This product was dissolved in water and refluxed with an ethanolic solution of the stoichiometric amount of picolinaldehyde. On cooling the mixture, the desired substance was obtained. The product was recrystallized from ethanol. It formed brown needles, stable in air (m.p. 212–4°; found: C 36.9%; H 3.5%; N 24.9%: calculated for $C_7H_8N_4Se$: C 36.85%; H 3.53%; N 24·56%).

NAT. Nicotinaldehyde thiosemicarbazone was obtained commercially.

Solubility

PAT and PASE are soluble in acetone and methanol, moderately soluble in ethanol, and sparingly soluble in water, chloroform, nitrobenzene and carbon tetrachloride.

Infrared spectra

Infrared spectra were obtained in nujol suspension, and the bands assigned to the stretching vibrations of -NH- (3500–3000 cm^{-1}), >C=N (1630–1515 cm^{-1}), >C=S (1130–1010 and 830–805 cm^{-1}) and >C=Se (1110–720 cm^{-1}) groups. The most characteristic bands of the last two groups were at 820 and 770 cm^{-1} for PAT and PASE, respectively.

Ultraviolet spectra

The ultraviolet absorption spectra for reagent in water and ethanol media showed similar maximum between 300 and 350 nm. Bathochromic shifts were produced on changing from water to ethanol as solvent (from 312 to 323 nm for PAT and from 320 to 335 nm for PASE). The solutions decomposed in time, PAT slowly and PASE faster. The effect of pH on the spectra is shown in Figs. 1 and 2.

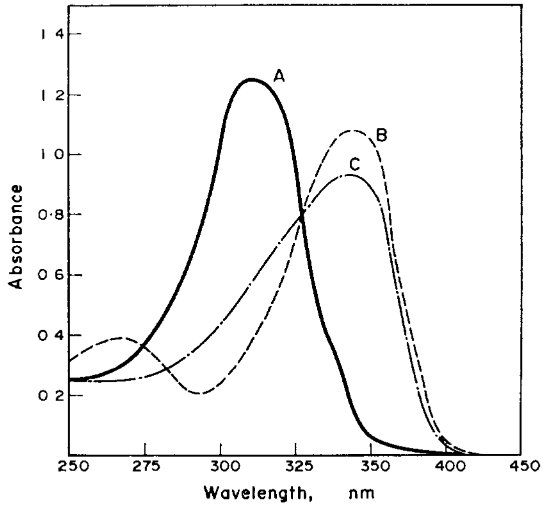


FIG. 1.—Absorption spectra of PAT (4 × 10^{-5} M in water) at pH 7·2 (*A*), 12·8 (*B*) and 1·3 (*C*).

NAT behaved similarly to PAT and PASE (bathochromic shifts at pH < 4 or > 10), but BAT gave a shift only in alkaline medium.

Determination of ionization constants

The Phillips and Merritt method[7] was used with 2 × 10^{-3}M ethanolic solutions. Table I gives the results.

Action of reducing and oxidizing agents

Reducing agents in moderate concentrations did not alter the absorption spectra of PAT and PASE, but oxidizing substances did. PAT was oxidized in different ways, depending on the pH; PASE always gave the same final form (also given on aerial oxidation of the solution for 7–8 days). The oxidation of PASE was reversible. Attempts to isolate the oxidation products were unsuccessful.

Reactions with cations

The reaction of PAT, PASE and NAT with 40 cations, up to concentrations of 1000 ppm, at various pH values, was investigated. As(III) or (V), Sn(II) or (IV), Pt(IV), Al, Cr(III), Be, UO$_2$(II)

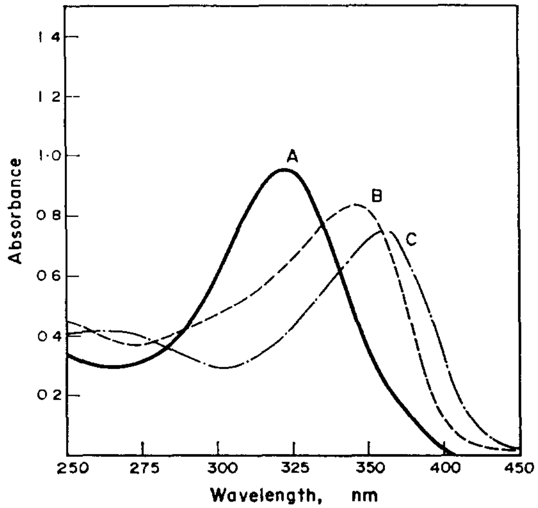


FIG. 2.—Absorption spectra of PASE ($4 \times 10^{-5}M$ in water) at pH 6·9 (*A*), 12·8 (*B*) and 1·2 (*C*).

TABLE I.—VALUES OF IONIZATION CONSTANTS

Substance	pK_b	pK_a
Picolinaldehyde thiosemicarbazone	9·40	9·75
Picolinaldehyde selenosemicarbazone	9·80	9·60
Nicotinaldehyde thiosemicarbazone	9·60	10·40
Benzaldehyde thiosemicarbazone	—	11·30

Th, La, Ce(III), W(VI), Mo(VI), alkaline and alkaline earth metals did not react. Zn and Mn(II) reacted with PAT and PASE in alkaline medium only.

The reactions of PAT and PASE were very similar, but the PASE complexes were more highly coloured and the sensitivity lower. In many cases, red precipitates of elementary selenium appeared soon after the solutions had been prepared. The most sensitive reactions (pD > 5) were those of Co(II), Fe(II) and (III), Ni and Cu(II). With Pd(II), Au(III) and V(V) an orange-yellow colour was produced (pD 5·4, 4·0 and 5·7 respectively). Bi and Sb(III) gave a weak yellow colour, as did Ag and Pb. Hg(I) and Hg(II) formed yellowish-white precipitates.

NAT reacts with Hg(I) and Hg(II) (yellowish precipitates), Cu(II) (green colour) and Pd(II) (yellow colour). The last was the most sensitive (pD 5·4 at pH 3–5).

The PASE complexes of Fe(II), Fe(III), Ce(II), Ni and Cu(II) were investigated in the same way as the PAT complexes. The results are given in Table II, with those for PAT for comparison.

The Cu(II) complex was very unstable, red precipitates of elementary selenium being formed a

TABLE II.—CHARACTERISTICS OF PAT AND PASE COMPLEXES IN SOLUTION

	Picolinaldehyde thiosemicarbazone				Picolinaldehyde selenosemicarbazone			
Cation	Optimum pH	λ, *nm*	ε, *l.mole*$^{-1}$.*cm*$^{-1}$	M:R	Optimum pH	λ, *nm*	ε, *l.mole*$^{-1}$.*cm*$^{-1}$	M:R
Co(II)	5·6–9·5	356	14×10^3	1:2	8·7–12·1	435	$5·5 \times 10^3$	1:2
		410	$7·4 \times 10^3$					
Ni(II)	7·2–10·7	385	19×10^3	1:2	5·5–10·5	400	$10·7 \times 10^3$	1:2
Fe(III)	3·9–7·9	360	14×10^3	1:2	3·5– 7·0	445	$6·8 \times 10^3$	1:2
Fe(II)	9·4–12·3	610	$5·8 \times 10^3$	1:3	9·8–12·0	615	$6·9 \times 10^3$	
Cu(II)	8·9–10·7	360	22×10^3	1:1		388		

few minutes after preparation of the samples. The Ni complex was stable for 1 hr and then decomposed slowly. The other three complexes were stable for at least 5 hr. The effect of pH on the oxidation rate of the green Fe(II) complex to the yellow Fe(III) complex was studied for both reagents. The results are shown in Table III.

TABLE III.—TIME NEEDED TO OXIDIZE THE FERROUS COMPLEXES

pH	Fe(II)-PAT *hr*	Fe(II)-PASE *hr*
4·5	0·3	0·1
5·0	1·5	0·2
6·2	3·5	0·2
6·5	4·0	0·3
8·5	21·0	0·4
10·0	40·0	
12·0	43·0	

The Fe(II)-PASE complex was extracted more easily into chloroform than the Fe(II)-PAT complex, although it was stable in this medium for only 1·5–2 hr. The PAT complex was stable for 5 hr. Ascorbic acid prevents the oxidation of these complexes in aqueous solution.

DISCUSSION

The infrared spectra agreee with those described by Gingras *et al.* for thiosemicarbazones[8–10] and selenosemicarbazones.[11] The band at 820 cm^{-1} in the picolinaldehyde thiosemicarbazone spectrum disappears when the complexes are formed,[3] showing that the sulphur atom is involved in the formation of these complexes.

The bathochromic shift in alkaline medium can be considered as due to the greater resonance[8] of the form $—N{=}\underset{\displaystyle S^-}{\underset{|}{C}}—NH_2$, which has the conjugated $—HC{=}N—N{=}C\lt$ group as chromophore. The bathochromic shift in acid medium may be due to protonation of the nitrogen atom in the pyridine ring, as it does not appear in benzaldehyde thiosemicarbazone, and has a very similar value to that of pyridine and its derivatives.[12] That pK_a for PAT is higher than that of PASE agrees with Volka and Holzbecher's results[13] for salicilaldehyde thiosemicarbazone and selenosemicarbazone.

The oxidation of selenosemicarbazone to a form with maximum absorption at 287 nm may be explained as due to formation of a diselenide, based on the tendency of compounds with $\gt C{=}Se$ or $\gt C{=}S$ groups to dimerize to the form $+—\overset{\diagdown}{\underset{\diagup}{C}}—Se—Se—\overset{\diagup}{\underset{\diagdown}{C}}+$;[14,15] unfortunately, the rapid decomposition of the product precludes its study.

An interesting difference between the behaviour of nicotinaldehyde and benzaldehyde thiosemicarbazone and of PAT and PASE is that the former two hydrolyse in acid medium, but the latter two do not. This again reveals the different character of positions 2 and 3 of the pyridine ring. Another important characteristic is that PAT is much more reactive than NAT with cations. NAT has important reactions only with Pd(II) and Cu(II), behaviour similar to that of other thiosemicarbazones in which the group attached to the thiosemicarbazide does not have a free electron pair (benzaldehyde, acetone, *etc*). Increased separation of the thiosemicarbazide group from the pyridine ring prevents the latter from participating in the formation of the complexes.

Department of Analytical Chemistry
University of Seville
Seville, Spain

J. M. CANO PAVON
F. PINO

Summary—The analytical properties of picolinaldehyde thiosemicarbazone and selenosemicarbazone have been studied, in order to investigate the changes produced when the Se atom is substituted for the S atom. The ionization constants of both substances are very similar. The complexes of picolinaldehyde selenosemicarbazone with cations in aqueous solution are less stable, and the absorption spectra show bathochromic and hypochromic shifts. The introduction of the Se atom offers no advantages in the analytical application of these compounds.

Zusammenfassung—Die analytischen Eigenschaften des Thiosemicarbazons und des Selenosemicarbazons von Picolinaldehyd wurden untersucht, um die Änderungen bei Substitution des S-durch ein Se-Atom zu erfassen. Die Ionisationskonstanten beider Substanzen sind sehr ännlich. Die Komplexe von Picolinaldehyd-Selenosemicarbazon mit Kationen in wäßriger Lösung sind weniger stabil und ihre Absorptionsspektren zeigen bathochrome und hypochrome Verschiebungen. Die Einführung des Se-Atoms bietet bei der analytischen Verwendung dieser Verbindungen keine Vorteile.

Résumé—On a étudié les propriétés analytiques de la thiosemicarbazone et de la sélénosemicarbazone de l'aldéhyde picolinique, afin d'examiner les changements produits quand l'atome de Se est substitué à l'atome de S. Les constantes d'ionisation des deux substances sont très similaires. Les complexes de la sélénosemicarbazone de l'aldéhyde picolinique avec les cations en solution aqueuse sont moins stables, et les spectres d'absorption montrent des déplacements bathochromes et hypsochromes. L'introduction de l'atome de Se n'offre pas d'avantages dans l'application analytique de ces composés.

REFERENCES

1. J. M. Cano Pavon, D. P. Bendito and F. Pino, *An. Quimica*, 1969, **65**, 667.
2. *Idem, ibid.*, 1971, **67**, 299.
3. J. M. Cano Pavon, J. Vazquez Aller, D. P. Bendito and F. Pino, *Inf. Quim. Anal.*, 1971, **25**, 149.
4. J. M. Cano Pavon, *Ch.D. Thesis*, Seville, 1971.
5. A. V. Ablov and N. I. Belichuk, *Zh. Neorgan. Khim.*, 1969, **14**, 179.
6. R. Huls and M. Renson, *Bull. Soc. Chim. Belges*, 1956, **65**, 511.
7. J. P. Phillips and L. L. Merritt, *J. Am. Chem. Soc.*, 1948, **70**, 410.
8. B. Q. Gingras, R. L. Somorjai and C. H. Bayley, *Can. J. Chem.*, 1961, **39**, 973.
9. D. M. Wiles, B. A. Gingras and T. Suprunchuk, *ibid.*, 1967, **45**, 469.
10. D. M. Wiles and T. Suprunchuk, *ibid.*, 1967, **45**, 2258.
11. B. A. Gingras, T. Suprunchuk and C. H. Bayley, *ibid.*, 1965, **43**, 1650.
12. H. C. Brown and D. H. McDaniel, *J. Am. Chem. Soc.*, 1955, **77**, 3752.
13. K. Volka and Z. Holzbecher, *Collection Czech. Chem. Commun.*, 1969, **34**, 3160.
14. A. Chiesi, G. Grossoni, M. Nardellio and M. E. Vidoni, *Chem. Commun.*, 1969, **D8**, 404.
15. R. S. Ramakrishna and H. M. N. H. Irving, *Anal. Chim. Acta*, 1969, **48**, 251.

Talanta, 1972, Vol. 19, pp. 1665 to 1669. Pergamon Press. Printed in Northern Ireland

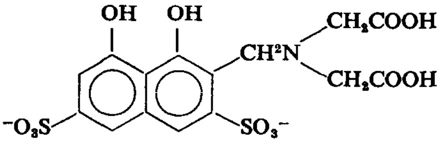
ANNOTATIONS

On the nature of so-called "Khimdu"

(*Received* 24 *April* 1972. *Accepted* 18 *May* 1972)

THE methyliminodiacetic acid derivative of chromotropic acid (disodium salt of 1,8-dihydroxynaphthalene-2*N*,*N*-dicarboxymethylaminomethyl-3,6-disulphonic acid, so-called "Khimdu") was first reported by Basargin *et al.* as a colorimetric reagent for titanium(IV).[1]

As we have been interested in this type of reagent, we tried to repeat their work carefully, but found some doubts about the nature of the reported compound. According to the result of our investigation, it is very likely that the reported reagent is a mixture of various reaction products, and not the pure compound having the proposed chemical structure(I).



(I)

EXPERIMENTAL

Reagents

Buffer solutions of hydrochloric acid/potassium chloride (pH 2), hexamethylenetetraamine/hydrochloric acid (pH 3) and potassium acetate/acetic acid (pH 5) were used.

Metal ion stock solutions (0·01*M*) were prepared from analytical grade ferric nitrate and metallic titanium, and their strengths were determined by EDTA titration. The stock solutions were diluted with distilled water before use.

Apparatus

A column 16 mm in diameter and 500 mm long was used for the gel chromatographic separation of the reaction mixture. The column was filled with a Sephadex LH-20 gel which had been swollen in the eluent (80% aqueous methanol) for 24 hr before use.

Electronic spectra were observed with a Hitachi 124 double-beam recording spectrophotometer.

Synthesis of Khimdu

Khimdu was synthesized according to the method of Basargin.[2] A mixture of 4·37 g (0·12 mole) of chromotropic acid (disodium salt) and 1·6 g (0·012 mole) of iminodiacetic acid was placed in a 100-ml reaction flask. After addition of 20 ml of water, the mixture was heated on a water-bath until dissolution was complete. The solution was cooled to about 50°, and the pH adjusted to 2·0–3·0 with 1*M* hydrochloric acid. Then 0·87 ml (0·012 mole) of 37% formaldehyde was added while stirring for several minutes. The reaction mixture was kept at room temperature for 3 hr, then transferred into a 300-ml beaker, and 120 ml of acetone were added to precipitate the product. The solution at first, gave a white suspension, from which a reddish-brown heavy oil separated. After collection, the oily product was treated with acetone to yield a brown powder.

The product was carefully pulverized under acetone, then filtered off, washed with acetone and ether successively, and finally dried over phosphorus pentoxide. The yield of the crude product was 5·25–5·88 g (86–96%) (product KA).

In an alternative procedure, the mole ratio of the reagents was altered to 1:2:3, and the reaction was carried out at 50° in an atmosphere of nitrogen for 14 hr. The reaction product was treated in a similar fashion to that described above, and a reddish brown powder (product KB) was obtained (yield: 73%).

Chromatographic fractionation of the reaction products

In order to purify the crude reaction products, samples of KA and KB were subjected to chromatographic fractionation on a Sephadex LH 20 gel column at an elution speed of 0·3 ml/min. The effluents were fractionated into three or four fractions according to their relative differences in ultraviolet absorption spectra. Each fraction was concentrated to a small volume under reduced pressure, and pure product precipitated with acetone. The isolated product was washed with acetone and ether, and vacuum-dried.

The yields of fractions obtained were as follows: 100 mg of KA gave 8·2 mg of KA-(1), 44·4 mg of KA-(2) and 9·1 mg of KA-(3), and 150 mg of KB gave 1·0 mg of KB-(1), 66·5 mg of KB-(2), 7·4 mg of KB-(3) and 10·5 mg of KB-(4).

The purified sample as well as the crude products were subjected to the absorption spectral analysis and elemental analysis.

RESULTS AND DISCUSSION

Our original purpose was to reproduce Basargin's results, and the samples obtained were found to have spectral characteristics identical with those of Khimdu. It is seen from Figs. 1, 2 and 3, that the crude product KA gave an absorption spectrum which is very close to that of Khimdu, and the visible absorption spectra of iron(III) and titanium(IV) complexes of the product KA also showed identical characteristics with those of Khimdu. A continuous variation study of the iron(III) complex was also made in order to obtain an additional proof of identity of our sample with Khimdu. The results, as shown in Figs. 4 and 5, again confirmed the identity of our crude product with the material called Khimdu by Basargin, and the different metal ligand ratios obtained in the studies at different wavelengths also imply that more than one complex-forming species is present.

However, as the result of elemental analysis on the crude sample showed discrepancies from the expected value for Khimdu, the sample was purified. The sample was rather unstable, becoming darker at elevated temperature, and was very slightly soluble in most common organic solvents, so that purification by recrystallization did not seem to be feasible.

Of the chromatographic separations investigated, gel chromatography on Sephadex LH-20 column with 80% methanol as an eluent was found to give best separation. However, contrary to expectation, the absorption spectra of the fractionated samples became more divergent from those

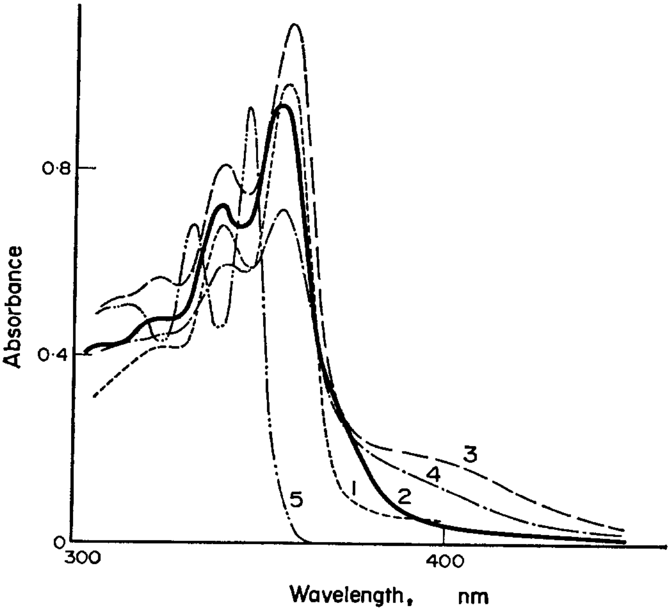


FIG. 1.—Visible absorption spectra of "Khimdu," the reaction products and chromotropic acid (reference water, 1-cm cells)

1, Khimdu 8 × $10^{-5}M$ (reproduced from ref. 1);
2, KA; *3*, KA-(2); *4*, KB-(2); *5*, chromotropic acid (all 1 × $10^{-4}M$).

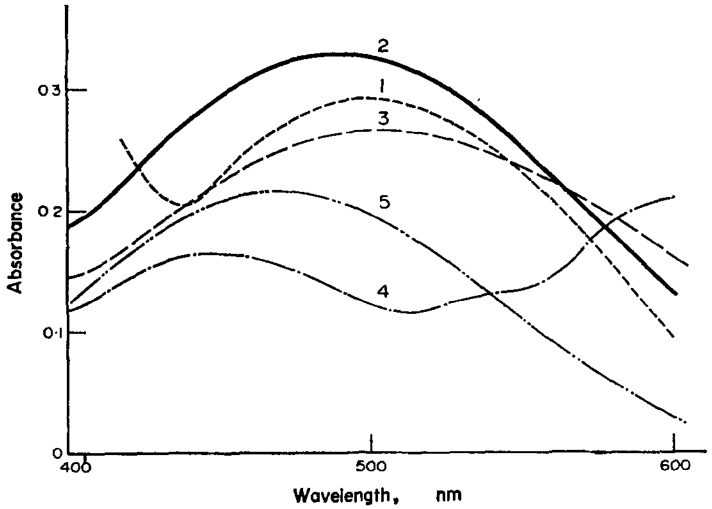


FIG. 2.—Visible absorption spectra of titanium(IV) complexes (reference reagent blank, 1-cm cells, pH 2)

1, Khimdu, 4 × $10^{-4}M$ and Ti 4 × $10^{-5}M$ (reproduced from ref. 1);
2, KA; *3*, KA-(2); *4*, KB-(2); *5*, chromotropic acid (all 1 × $10^{-4}M$ and Ti 4 × $10^{-5}M$).

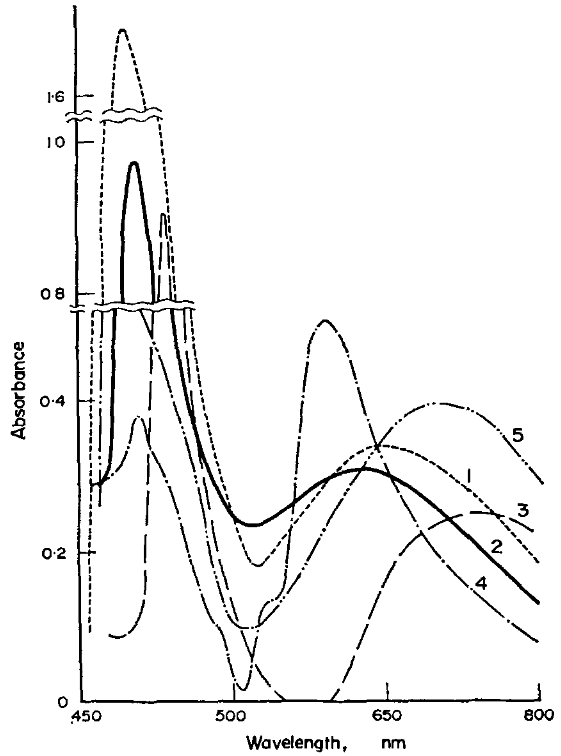


FIG. 3.—Visible absorption spectra of iron(III) complexes (reference reagent blank, 1-cm cells, pH 5).

1, Khimdu 2·5 × $10^{-3}M$ and Fe 2·5 × $10^{-4}M$ (reproduced from ref. 1);
2, KA; *3*, KA-(2); *4*, KB-(2); *5*, chromotropic acid (all 2·5 × $10^{-3}M$ and Fe(III) 2·5 × $10^{-4}M$).

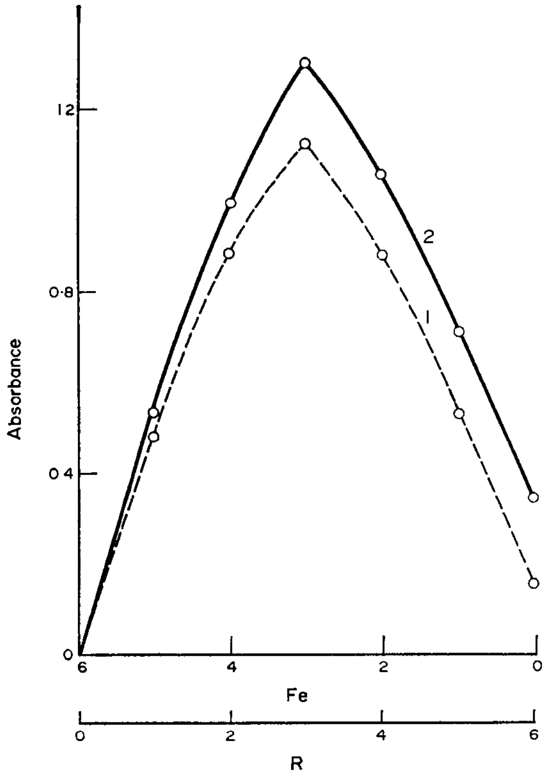


FIG. 4.—Continuous variation study on iron(III) complex at 400 nm. Total corcentration 1·0 × $10^{-4}M$; 1-cm cells; *1*, Khimdu, at 395 nm and pH 3·0 (reproduced from ref. 1); *2*, KA, at 403 nm and pH 2·0.

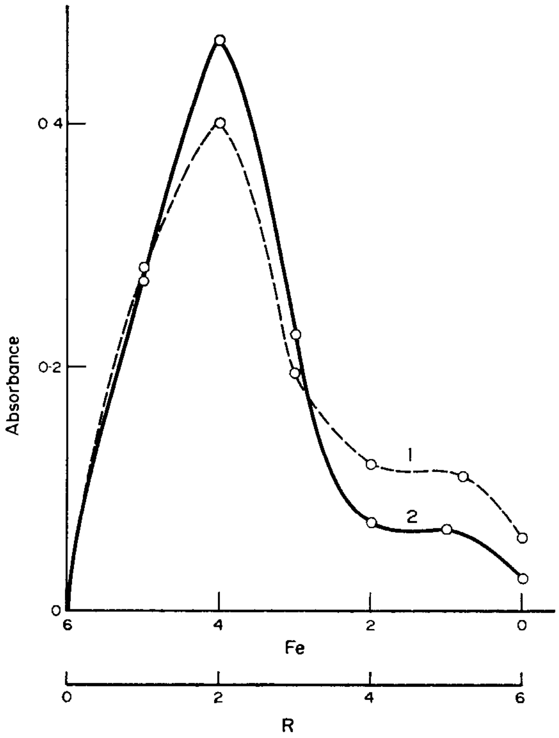


FIG. 5.—Continuous variation study on iron(III) complex at 650 nm Total concentration 2·0 × $10^{-4}M$, 5-cm cells; *1*, Khimdu, at 650 nm and pH 3·0 (reproduced from ref. 1); *2*, KA, at 630 nm and pH 2·0.

of Khimdu. Moreover, the results of elemental analyses on the fractionated samples deviated more and more from the calculated values for Khimdu, as shown in Table I. In the case of KB, where the mole-ratio of the reactants was 1:2:3, the nitrogen content in the product as well as in the chromatographed fractions was higher than for KA. However, none of the results for the fractions agree with the calculated value for Khimdu. Generally, as the fractionation goes on, the nitrogen content becomes lower. For example, the fraction KA-(2) does not contain nitrogen and the analytical value is rather close to that of the dimethylol derivative of chromotropic acid.

TABLE I.—ELEMENTAL ANALYSES OF THE CRUDE PRODUCTS AND THE CHROMATOGRAPHED FRACTIONS

Sample	C%	H%	N%	Na%
KA	36·0	3·2	2·0	8·2
KA-(1)	34·6	3·1	0·7	8·8
KA-(2)	34·7	2·6	0·0	9·5
KA-(3)	33·4	2·8	0·2	10·5
KB-(1)	37·8	3·6	3·1	6·0
KB-(2)	35·2	3·3	2·6	9·3
KB-(3)	—	—	1·6	—
KB-(4)	—	—	0·5	—
Calcd. value for Khimdu ($C_{15}H_{13}NO_{12}S_2Na_2$)	35·37	2·57	2·75	9·03
Chromotropic acid (sodium salt) ($C_{10}H_6O_8S_2Na_2$)	32·97	1·66	0·00	12·62
Dimethylol deriv. of chromotropic acid (sodium salt) ($C_{12}H_{10}O_{10}S_2Na_2$)	33·97	2·38	0·00	10·84

Although we do not want to give any decisive conclusion, as Basargin *et al.* did not show the analytical results for their sample, it is very likely that the product called "Khimdu" is not a compound with well-defined structure, but is a mixture of various reaction products.

YONG KEUN LEE*
KYU JA WHANG†
KEIHEI UENO

Department of Organic Synthesis
Faculty of Engineering
Kyushu University
Fukuoka 812, *Japan*

REFERENCES

1. N. N. Basargin, M. K. Akhmedli and M. M. Shirinov, *Zh. Analit. Khim.*, 1968, **23**, 1813.
2. N. N. Basargin and M. I. Starostina, U.S.S.R. Patent 175514 (Cl. C07c), Oct. 9, 1965.

Summary—The reagent called "Khimdu" has been investigated and evidence found to show that it is not a pure compound but a mixture of several reaction products.

Zusammenfassung—Das Reagens "Khindu" wurde untersucht und Hinweise darauf erhalten, daß es sich nicht um eine reine Verbindung, sondern um ein Gemisch mehrerer Reaktionsprodukte handelt.

Résumé—On a examiné le réactif nommé "Khimdu" et trouvé des preuves montrant que ce n'est pas un composé pur mais un mélange de plusieurs produits de réaction.

---

* Colombo Project Fellow; present address: Department of Chemistry, College of Science and Engineering, Yonsei University, Seoul 120, Korea.

† Present address: Department of Manufacturing Pharmacy, College of Pharmacy, Sookmyung Women's University, Seoul 140, Korea

Talanta, 1972, Vol. 19, pp. 1670 to 1677. Pergamon Press. Printed in Northern Ireland

Zur Frage des Verlustes von Molybdän während der Analyse von metallischem Wolfram auf Molybdänspuren

(*Eingegangen am* 9. *Dezember* 1971. *Angenommen am* 10. *Januar* 1972)

TECHNISCHES Wolfram-Metall enthält stets Spurenverunreinigungen an Molybdän, in der Größenordnung zwischen 1000 und 10 ppm. Spezielle Anwendungsgebiete in der Elektronik und der Glühlampenfertigung erfordern einen möglichst geringen Molybdängehalt; damit eng verknüpft ist daher die Notwendigkeit einer exakten Methode zur analytischen Bestimmung dieser kleinen Gehalte neben überwiegend Wolfram.

In Fachkreisen bestehen derzeit sehr unterschiedliche Meinungen darüber, inwieweit bei einem der Bestimmung vorgeschalteten Glüh- bzw. Erhitzungsprozeß Molybdän infolge von Sublimation des Oxids verloren gehen kann. Um das Wolfram-Metall in Lösung zu bringen gibt es grundsätzlich zwei Vorbehandlungs-Möglichkeiten.

(1) Man oxidiert das Wolfram-Metall durch Glühen an Luft zu WO_3 und löst anschließend in Natriumhydroxidlösung. Um diesen Oxidationsvorgang in annehmbaren Zeiten durchführen zu können, werden Temperaturen von 750–850° vorgeschlagen.

(2) Man löst in einem Gemisch von Flußsäure und Salpetersäure, setzt danach Schwefelsäure zu und erhitzt entweder bis zum Auftreten von SO_3-Nebeln; meist wird aber bis zur Trockene eingedampft.

Im ersten Fall ist man sich uneinig darüber inwieweit MoO_3 unter diesen Glühbedingungen durch Sublimation flüchtig ist, im zweiten Fall wird die Bildung flüchtiger Oxyfluoride vermutet.

Wir haben nun diese beiden Varianten einer genauen Überprüfung im Hinblick auf Molybdän-Verluste unterzogen und sind dabei zu folgenden Ergebnissen gekommen.

(*a*) Ein oxidierendes Glühen von Wolfram-Metall an Luft bei 750° verursacht einen beträchtlichen Verlust an Molybdän, z.B. wurde der Gehalt von 350 auf 30 ppm herabgesetzt.

(*b*) Nach dem Lösen mit Flußsäure–Salpetersäure-Gemisch führt ein Erhitzen bis zur Verflüchtigung von SO_3 und auch ein Rösten nach vollständigem Abdampfen der Schwefelsäure bei 400° zu keinerlei Molybdän-Verlusten.

Diese Ergebnisse führen zu dem Schluß, daß die erste Vorbehandlungsvariante der Wolframproben vollkommen ungeeignet ist. Die zweite Arbeitsweise ist sicher und es besteht keine Gefahr von Molybdän-Verlusten. Letzteres wurde darüber hinaus von uns bereits in zwei Arbeiten bewiesen.[1,2]

Ergänzend muß erwähnt werden, daß bei oxidierendem Glühen von Wolfram-Metall auf Grund der exothermen Reaktion intermediär und lokal höhere Temperaturen auftreten werden, als der Ofentemperatur entspricht. Darüber hinaus dürfte auch die Kinetik der Oxidation des W-Mo-Mischkristalles eine Rolle spielen. Es ist anzunehmen, daß primär freies MoO_3 und WO_3 entstehen, die erst im weiteren Verlauf der Reaktion Oxidmischkristalle bilden.

Freies MoO_3 ist bekanntlich schon bei Temperaturen über 450° flüchtig. Sind hingegen die kleinen MoO_3-Mengen in das WO_3-Gitter eingebaut, so kann man ohne weiteres auf 750° erhitzen ohne daß Molybdän-Verluste auftreten. Dies wurde durch Glühversuche an einer Reihe von WO_3 Mustern, die auf Molybdän analysiert wurden, überprüft.

Versuchsanstalt
Metallwerk Plansee A.G.
A-6600 Reutte, Austria

E. LASSNER
H. SCHEDLE

Zusammenfassung—Es wird gezeigt, daß ein oxidierendes Glühen von Wolfram-Metall zu Wolframtrioxid zu einer Abnahme des Molybdängehaltes führt. Im Hinblick auf eine nachfolgende Molybdänbestimmung ist daher eine solche Glühung zu unterlassen. Hingegen ist beim Lösen von Wolfram in Fluß-Salpetersäuregemisch und anschließendem Abdampfen mit Schwefelsäure (bis zur Trockene) keine Verringerung des Molybdängehaltes zu verzeichnen.

Summary—It is shown that oxidative ignition of metallic tungsten to tungsten trioxide causes a decrease in the molybdenum content. Thus the ignition cannot be used when the molybdenum content is to be determined. On the other hand, when the tungsten is dissolved in a

mixture of hydrofluoric and nitric acids with subsequent fuming with sulphuric acid, no such decrease in the molybdenum content takes place.

Résumé—On a montré que l'ignition par voie oxydante du tungstène métallique en trioxyde de tungstène cause un décroissement de la teneur en molybdène. Une telle ignition doit donc être évitée lorsqu'il faut déterminer la teneur en molybdène. D'autre part, lorsque le tungstène est dissous dans un mélange d'acides fluorhydrique et nitrique avec traitement subséquent à l'acide sulfurique jusqu'à production de fumées, un tel décroissement de la teneur en molybdène ne se produit pas.

REFERENCES

1. E. Lassner, R. Püschel and K. Katzengruber, *Microchim. Acta*, 1970, 39.
2. E. Lassner and R. Püschel, *ibid.*, 1969, 527.

Louis Gordon Memorial Award 1970

Professor and Mrs. L. MEITES were presented with the Louis Gordon Memorial Award by Dr. HOWARD FRANCIS JR. (on left), for their paper on "Theory of Titration Curves—VII: The Properties of Derivative Titration Curves for Strong Acid–Strong Base and other Isovalent Ion-Combination Titrations" (*Talanta*, 1970, **17**, 525), which was judged to be the best-written paper published in *Talanta* in 1970.

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Recent Advances in Gas Chromatography: I. I. DOMSKY and J. A. PERRY (Eds.) Dekker, New York, 1971. pp. xi + 414. $19.50.

The book consists of the typescripts of 17 lectures presented at short courses on Gas Chromatography. The reproduction, which is in the modern style, serves to emphasise the origins of the book. Some authors quite clearly were more concerned with delivering a lecture whereas others were also concerned with publication (or providing those attending the lecture with a good paper whilst they spoke of something else). The book is inevitably a pot pourri of discussion and comment on various aspects of GLC such as columns, flow patterns, detectors, computer link-ups, silylation, and applications to the analysis of lipids, pesticides and metabolites. There are also two chapters on gel permeation chromatography.

Most of the chapters contain useful practical information and present it in a straightforward, well-illustrated manner, but overall the rigour demanded of formal papers or books is lacking. It provides a useful survey, and many workers may wish to consult specific chapters, but overall one is left with the impression that, whilst the lectures may have been informative and entertaining, on their translation into book form they should have been expanded and edited.

The Determination of Impurities in Nuclear Grade Sodium Metal: L. Silverman, Pergamon, Oxford, 1971. pp. ix + 143. £3.75, $10.00.

The book appears to be a collection of laboratory procedures for the determination of impurities in sodium metal and also sodium chloride, hydroxide and carbonate. Most emphasis is placed on carbon and oxygen but procedures for the determination of Al, Bi, B, Cd, Ca, Mg, Cs, Cl, Cr, Co, Cu, H, I, Fe, Pb, Li, Nn, Ni, P, K, Si, S and U are also given. There is little theory but the text abounds with practical wisdom, which may be appreciated by many analysts, since the procedures described have a general applicability. The descriptions of procedures are clear and likely pitfalls are pointed out.

Analytical Photochemistry and Photochemical Analysis: J. M. FITZGERALD (Ed.) Dekker, New York, 1971. pp. xiv + 360. $23.50.

The editors hope that the contributions in this volume will bring the developments of photochemistry with analytical implications to the attention of analytical chemists and provide photochemists with a critical survey of useful analytical methods. In view of the rapid growth of photochemistry the work is timely and stimulating. Several useful and unusual determinations are described in a series of reviews by various authors. These deal with lasers in analytical chemistry, actinometry, photochemical titrations and methods for studying the photolysis of polymers and co-ordination compounds, and other related topics.

Analytical Emission Spectroscopy, Vol. 1, Part 1; E. L. GROVE (Ed.), Dekker, New York, 1971. pp. xvi + 401. £12.60.

This is the first part of a projected three part work. Judgment of the whole will have to await the appearance of the whole, but in its own right the first part is most valuable. It contains long articles on the historical development of emission spectroscopy, the origins of atomic spectra, prisms, gratings, prism and grating instruments and spectroradiometric principles. There is little that is new in all this but the spacious accounts of fundamentals are welcome. If the other volumes match this the set will prove an invaluable tome of reference.

ANALYTICAL DATA

An essential but little acclaimed part of scientific research is the measurement of accurate values of the many constants used in the development and application of theory. Development work is usually thought of as interesting and exciting, and careful measurement by established methods as being dull and somehow less praiseworthy. The onlooker is sometimes left with the sneaking suspicion that this attitude sometimes arises because its holder lacks either the patience or the skill necessary for work of the highest accuracy. Be that as it may, it is quite certain that without the consolidation provided by the many careful workers who garner values for constants, theory would not progress very far and would not be nearly so useful as a guide to action. One of the problems of workers in this field is that of publication. Their results are usually of value in several fields of chemistry, but strictly speaking belong to none in particular. A consequence of this is that publication committees are often tempted to suggest submission to some other journal than their own, and authors experience difficulty in finding a medium for publication of their work. One of their difficulties is that journal space is already at a premium, and editors are naturally reluctant to occupy it with details of standard procedures applied to individual problems. We therefore propose to begin a new feature in *Talanta*, to be called "Analytical Data", which will serve for publication of such results with the minimum of background information. Once a pattern of experimentation has been established, a reference to it is all that is necessary to indicate how the work was done. Of course, if there is a new development discovered in the course of such work, that is a different matter, and it can be mentioned in more detail and itself become the reference point for future publications. In this issue we present the first papers in this feature. They are a little longer than we would normally expect, simply in order to set the pattern.

FOREWORD

ON THE occasion of the IUPAC International Congress on Analytical Chemistry and the 20th Anniversary of the founding of the Japan Society for Analytical Chemistry, it gives the Editorial Board and Publishers of *Talanta* great pleasure to mark the occasion and honour the work of Japanese analytical chemists by presenting this special issue containing invited contributions showing the wide range of interests and research in modern Japanese analytical chemistry.

The cover of this issue carries a transliteration of *Talanta* into Katakana characters.

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Zur Frage des Verlustes von Molybdän während der Analyse von metallischem Wolfram auf Molybdänspuren: E. LASSNER and H. SCHEDLE. (9 *December* 1971)

Complexation reaction of zirconium with chromogenic reagents—Calmagite and Solochrome Black 6B: C. P. GUPTA and K. N. MUNSHI. (20 *December* 1971)

Absorptiometric determination of palladium with 2,3-quinoxalinedithiol: J. A. W. DALZIEL and A. K. SLAWINSKI. (20 *December* 1971)

Determination of trace metals in water by X-ray fluorescence spectrometry: H. WATANABE, S. BERMAN and D. S. RUSSELL. (21 *December* 1971)

A semi-automatic system for operation of electrical detection for a spark-source mass-spectrometer: R. J. CONZEMIUS, W. A. RHINEHART and H. J. SVEC. (23 *December* 1971)

***o*-Amino-compounds of the heterocyclic azo dyestuffs as analytical reagents—II. Spectrophotometric determination of cobalt with 3-[(5-chloro-2-pyridyl)azo]-2,6-diaminopyridine:** S. SHIBATA, M. FURUKAWA and K. GOTO. (23 *December* 1971)

Direct determination of fluoride in aluminium reduction materials by use of an ion-selective electrode: THOMAS A. PALMER. (24 *December* 1971)

The complexes of Ag(I) with thiourea as ligand: A. BELLOMO, D. DE MARCO and A. DE ROBERTIS. (30 *December* 1971)

Distribution coefficients and cation-exchange selectivities of elements with AG50W-X8 resin in perchloric acid: F. W. E. STRELOW and H. SONDORP. (30 *December* 1971)

Spectrophotometric determination of osmium with 2R-acid in the presence of other platinum metals: B. V. AGARWALA and A. K. GHOSE. (30 *December* 1971)

Computer calculation of equilibrium constants by using program SCOGS; a further modification: I. G. SAYCE and V. S. SHARMA. (31 *December* 1971)

Méthode nouvelle de séparation des sulfates de strychnine et brucine: M. MARIAUD and D. HALOT. (31 *December* 1971)

Solvent extraction studies of indium(III): Separation from gallium(III): M. B. CHAVAN and V. M. SHINDE. (31 *December* 1971)

Acenaphthenequinone monoxime as a selective reagent for the spectrophotometric determination of platinum(IV) by solvent extraction: S. K. SINDHWANI and R. P. SINGH. (31 *December* 1971)

Microanalysis of sulphide, sulphite, sulphate and thiosulphate by thin-layer chromatography and ring-colorimetry: A. C. HANDA and K. N. JOHRI. (31 *December* 1971)

Bestimmung des Komplextypus von dissoziierten Komplexen mit Hilfe transformierter Titrationskurven: J. BORÁK, Z. SLOVÁK and J. FISCHER. (5 *January* 1972)

Applications involving the iodide ion—X. Determination of copper and analysis of its mixtures with some other cations: H. KHALIFA and E. A. EL-GAZZAR. (5 *January* 1972)

Selective detection of bismuth(III) and iron(II) with certain new reagents: G. S. JOHAR. (5 *January* 1972)

New tests for the detection of azide: G. S. JOHAR. (5 *January* 1972)

The application of photon counting in atomic-absorption spectrophotometry: R. M. DAGNALL, B. L. SHARP and T. S. WEST. (14 *January* 1972)

On the problem of increasing the sensitivity of anodic stripping voltammetry: LUDMILA HUDEROVÁ and KAREL ŠTULÍK. (18 *January* 1972)

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Rapid colorimetric determination of indoxyl acetate: R. J. Nadalin. (31 *October* 1971)

Trennungsfreie Bestimmungen der Erdalkalimetalle—Calcium, Strontium, Barium—mit Hilfe der AAS: Gerhard M. Neumann. (5 *November* 1971)

Precipitation of barium chromate in the presence of strontium and lead by complexation followed by volatilization of ammonia: F. H. Firsching and Paul H. Werner. (9 *November* 1971)

Reversible electrode reactions: Reduction of Cd–malonate–oxalate complex at the D.M.E.: S. C. Khurana and C. M. Gupta. (18 *November* 1971)

Nouvelle microméthode colorimétrique pour le dosage des nitrites: Camelia Ghimicescu and Vasile Dorneanu. (23 *November* 1971)

Formation of nickel, cobalt(II), manganese(II) and cadmium ferrocyanides—II: Athos Bellomo, Domenico De Marco and Agatino Casale. (23 *November* 1971)

Gallacetophenone as an analytical reagent for tantalum: R. Raghava Naidu. (29 *November* 1971)

Extraction with long-chain amines—VI. Polarographic determination of uranium: Rudolf Přibil, Jr. and Jiří Adam. (30 *November* 1971)

Selective extraction and spectrophotometric determination of copper as phenylacetate: Jiří Adam and Rudolf Přibil. (30 *November* 1971)

Analytical chemistry in Japan: Taitiro Fujinaga. (1 *December* 1971)

A general multiparameter least-squares curve-fitting computer program and some of its applications: Thelma Meites and Louis Meites. (1 *December* 1971)

Study of chromium hydroxide precipitated from homogeneous solution: M. N. Sastri and J. Rajagopala Rao. (2 *December* 1971)

Determination of and differentiation between cassiterite and silicate-lattice-bound tin in silicate rocks containing traces of tin: J. Agterdenbos and J. Vlogtman. (5 *December* 1971)

Spectrophotometric determination of copper in alkaline solutions and evaluation of some hydroxy-substituted 1,10-phenanthrolines as chromogenic reagents: W. E. Dunbar and A. A. Schilt. (6 *December* 1971)

Cation-exchange separation of alkaline earths, using mixed solvent eluents: R. P. Bhatnagar and S. L. Garde. (6 *December* 1971)

Candoluminescence—a new flame technique for trace analysis—I. Determination of bismuth: R. Belcher, S. Bogdanski and A. Townshend. (6 *December* 1971)

Photometric complex-formation titrations of submicromole amounts of metals—III. Back-titrations: J. Kragten. (10 *December* 1971)

A simple non-selective detector for gas-phase chromatography, using the measurement of reflected microwave power: R. M. Dagnall, M. D. Silvester, T. S. West and P. Whitehead. (10 *December* 1971)

Indirect atomic-absorption spectrophotometry for determination of ppM levels of arsenic by combustion of MIBK extract of arsenomolybdic acid: Y. Yamamoto, T. Kumamaru, Y. Hayashi, M. Kanke and A. Matsui. (13 *December* 1971)

Modifications of the computer programme SCOGS: W. A. E. McBryde and J. L. McCourt. (13 *December* 1971)

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming the following new members to the Advisory Board of the journal.

A. CORSINI J. JORDAN
F. BERMEJO-MARTINEZ
L. E. SMYTHE A. TOWNSHEND

They also wish to record their sincere thanks for the help given by

M. L. DIMBAT S. GREENFIELD
K. J. KARRMAN K. ISSLEIB
R. E. SIEVERS W. SIMON
E. STAHL

who retire from the Advisory Board.

PROFESSOR ALFIO CORSINI was born in Hamilton, Ontario in 1934, and graduated from McMaster University, B.Sc. in 1956 and Ph.D. in 1961. He worked as Research Associate with Professor Freiser in Arizona from 1961 to 1963 and has served on the staff of McMaster University since, first as Assistant Professor, and as Associate Professor since 1968. His research interests are the chemistry of analytically useful chelates, especially factors affecting selectivity, complexes of oxine and its derivatives, and trace analysis by fluorescence and atomic-absorption methods. He is married, with two children, and his hobbies are gardening, athletics and reading.

JOSEPH JORDAN, M.Sc., Ph.D., is a Professor of Chemistry at the Pennsylvania State University, where he has chaired the analytical area committee since 1960. He has authored and co-authored about a hundred research papers, and several authoritative reviews on electroanalytical chemistry, thermochemical titrimetry and enthalpimetric analysis. Professor Jordan's contributions include: development of hydrodynamic voltammetry, direct injection enthalpimetry, thermo-kinetic analysis and gas enthalpimetry; the use of mixed carrier gases in gas chromatography and quantitation based on considerations of kinetic theory; thermometric enthalpy titrations in molten salts; kinetics and mechanisms of electrode reactions and electron transfer; electrochemical models of haemoproteins; calorimetric titrations of antibodies and antigens and the thermochemistry of immunological processes; polarography, rotating disk electrode voltammetry and redox chemistry in fused salts at elevated temperatures.

Professor Jordan has served as chairman (1967–71) of the Commission on Electrochemistry of the International Union of Pure and Applied Chemistry (IUPAC) and is currently a titular member of IUPAC's Physical Chemistry Division Committee.

PROFESSOR F. BERMEJO-MARTINEZ was born in Corunna, Spain. He studied chemistry and pharmacy at the Santiago de Compostela University in Spain, where he got his diploma with *extraordinary prize* in 1943. A few years later he took his Doctor of Chemical Sciences degree, *cum laude* at the Madrid University in 1948. After completing his university studies he worked with Professor J. González-Carreró in the "Montequi Institute for Inorganic and Analytical Chemistry" of the Faculty of Pharmacy in Santiago de Compostela as Assistant Professor. In 1950 he became Professor of Analytical Chemistry at Oviedo University, and in 1951 in the Faculty of Sciences of Santiago de Compostela University. He is now Head of the Analytical Department in this University and Chief of the Analytical Chemistry Section of the High Conseil Scientific Research in Santiago de Compostela. His main scientific activities are in the field of analytical applications of EDTA and analogous reagents and in microanalysis. His book *Analytical Applications of EDTA and Analogues*, though published in Spanish, is well known to specialists throughout the world. He is a member of 16 scientific societies in Spain and abroad. His academic books *Handbook of Quantitative Analytical Chemistry* and *Numerical Calculations in Analytical Chemistry* are used by many students and professional analysts. His editorial activity comprises 8 books and translations from English, French and German, and he is the founder and editor of the *Acta Científica Compostelana*. His scientific publications number about 140, half on analytical applications of EDTA *etc*, and half in other fields of analytical chemistry. He is married and has nine children (4 boys and 5 girls) aged between 21 and 7 His hobbies are scientific documentation, gardening, and swimming.

DR. ALAN TOWNSHEND has been a lecturer in Analytical Chemistry at the University of Birmingham since 1966, where he had obtained the degrees of B.Sc. (1960) and Ph.D. (1963). After spending one year as a Research Fellow with Dr. Louis Gordon at Cleveland, he returned to Birmingham as an Assistant Lecturer in 1964. His research interests are in catalytic and enzymatic methods of trace analysis, gravimetry, solution and flame spectroscopy, polarography and many other aspects of analytical chemistry. Dr. Townshend is Hon. Treasurer of the Midlands Region of the Society for Analytical Chemistry and Recorder of the Midlands Association for Qualitative Analysis.

Professor Lloyd E. Smythe graduated in Australia and did research at Cambridge before joining the Analytical Group at Harwell. After working with A. A. Smales for several years he was appointed as Head of the Analytical Group of the Australian Atomic Energy Commission Establishment at Lucas Heights. He left that position in 1969 to become the first Professor of Analytical Chemistry in an Australian University, the University of New South Wales. There he has built up a flourishing research group working on trace analysis by flame spectroscopy and spectrofluorimetry, on analytical instrumentation, and on instrument design. He was elected Federal President of the Royal Australian Chemical Institute in 1970.

LOUIS GORDON MEMORIAL AWARD

Dr. Chalmers presenting the 1971 Louis Gordon Memorial Award to Dr. Sue Humphries and Dr. Gordon Briscoe

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Stepwise formation of bivalent metal complexes with 4-hydroxy-3-oximinomethylazobenzene: P. N. Mohan Das, O. P. Sunar and C. P. Trivedi. (5 *June* 1972)

Acid-base equilibria in ethylene glycol—I. Definition of pH and determination of p*K*-values of acid-base indicators: P. Zikolov and O. Budevsky. (19 *June* 1972)

Separation of lithium from Dead Sea brines by gel-permeation chromatography: M. Rona and G. Schmuckler. (19 *June* 1972)

Amperometrische Bestimming der Metalle unter Anwendung von Thioacetamid—XI. Untersuchungen über Cu_2S-Bildungsgeschwindigkeit in Ammoniakalischen Cu^+-Ionen Lösungen mittels Thioacetamid: Maria Pryszczewska. (19 *June* 1972)

Atomic-absorption and emission spectrometry of mercury at 184·9 nm: R. M. Dagnall, J. M. Manfield, M. D. Silvester and T. S. West. (20 *June* 1972)

Potentiometric determination of stepwise stability constants of vanadium, molybdenum and tungsten chelates formed with asparagine and glutamine: R. C. Tewari and M. N. Srivastava. (20 *June* 1972)

Comparison of the ion-exchange behaviour of zirconium, thorium, vanadium, uranium, stannic and titanium tungstates: Mohsin Qureshi, Jai Prakash Gupta and Veenz Sharma. (20 *June* 1972)

Extraktion der Metallionen Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) mit geschmolzenem Oxin und Bestimmung der extrakierten Metalle mit Hilfe von Röntgenfluoreszenz: B. Magyar and F. I. Lobanov. (20 *June* 1972)

Extractive spectrophotometry of the molybdenum(III) 1,10-phenanthroline thiocyanate and 2,2′-dipyridyl thiocyanate complexes: Amal Kanti Bhadra and Siddheswar Banerjee. (21 *June* 1972)

Indirect atomic-absorption determination of boron by solvent extraction as the tris(1,10-phenanthroline) cadmium–tetrafluoroborate ion-pair: Y. Hayashi, S. Matsushita, T. Kumamaru and Y. Yamamoto. (26 *June* 1972)

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Logarithmic diagrams and Gran-curves as an aid in potentiometric titrations in complexometry: Axel Johansson. (18 *March* 1972)

Preparation and infrared spectra of palladium derivatives of some organophosphorus insecticides: T. F. Bidleman and R. W. Frei. (1 *May* 1972)

Atomabsorptionspektralphotometrische Bestimmung von Zink in Galliumarsenid und Galliumaluminiumarsenid: K. Dittrich and W. Zeppan. (3 *May* 1972)

Thermal, X-ray and neutron-activation investigation of compounds of niobium and tantalum: Fadhil Jasim. (17 *May* 1972)

Analysis of metals by solid–liquid separation after liquid–liquid extraction. Spectrophotometric determination of cadmium by extraction of cadmium oxinate with naphthalene: Masatada Satake. (22 *May* 1972)

Bestimmung ^{35}S-markierter Polythionate nach hochspannungsionophoretischer Trennung: E. Blasius and H. Wagner. (23 *May* 1972)

A proposed sampling constant for use in geochemical analysis: C. O. Ingamells and P. Switzer. (23 *May* 1972)

Potassium thiocarbonate (PTC) as a precipitant for osmium and iridium: K. N. Johri, N. K. Kaushik and Kiran Bakshi. (25 *May* 1972)

The acid stability constants of Alizarin Fluorine Blue: Folke Ingman. (27 *May* 1972)

The indirect polarographic determination of tripolyphosphate ions in the presence of other polyphosphates, with oxtyltin chloride: S. Shaw and A. Townshend. (29 *May* 1972)

A new titrimetric method: Thermoradiometric titration: J. Tölgyessy and J. Lesný. (30 *May* 1972)

Enthalpimetry of non-aromatic alkenes: D. W. Rogers and R. J. Sasiela. (30 *May* 1972)

Rapid chelometric determination of lead in lubricating oil *via* mercaptoacetate extraction: Samaresh Banerjee and R. K. Dutta. (7 *June* 1972)

Talanta 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Determination of metals in organo-lanthanide compounds by the oxygen-flask method: P. Bonda, A. E. Crease and P. Legydins. (30 *March* 1972)

Raman spectrometric studies of aqueous borate complexes with ethylene glycol and mannitol: John Knoeck. (12 *April* 1972)

Metal complexation with 2-hydroxy-6-methylpyridine-3-carboxylic acid: Veena Kushwaha, R. P. Singh and Mohan Katyal. (21 *April* 1972)

Macro and semimicro infrared determination of nitrogen in raw nitrocellulose and nitrocellulose contained in propellants: George Norwitz and David E. Chasan. (21 *April* 1972)

Determination of phosphorus in phosphazenes and phosphines: Sanford L. Erickson. (24 *April* 1972)

Cadmium and silver sulphide-impregnated silicone rubber membranes as selective electrodes for cadmium ions: Hiroshi Hirata and Kenji Date. (24 *April* 1972)

On the nature of so-called "Khimdu": Yong Kuen Lee, Kyu Ja Whang and Keihei Ueno. (24 *April* 1972)

Limitations in Bishop's treatment and application of indicator parameters with reference to redox indicators: K. Sriramam. (26 *April* 1972)

Uses of liquid ion-exchangers in inorganic analysis: H. Green. (1 *May* 1972)

Determination of small amounts of water with coulometrically generated Karl Fischer reagent: Ronald Karlsson. (1 *May* 1972)

Pyrazine-2,3-dicarboxylic acid as an analytical reagent: Spectrophotometric determination of iron(II): G. S. Sanyal and S. Mookherjea. (3 *May* 1972)

Hydrogen peroxide formation upon oxidation of oxalic acid in presence and absence of oxygen and of manganese(II)—III. Iron(III) and copper(II) as retarders: I. M. Kolthoff, E. J. Meehan and Masaru Kimura. (5 *May* 1972)

Iron(II)—chloramine-T reaction: V. R. S. Rao and G. Aravamudan. (8 *May* 1972)

Nouvelle microméthode colorimétrique pour la détermination de l'ion I^-, comme microélement, dans des eaux et des produits organiques: Camelia Chimicescu, Maria Stan and Mujor Dragomir. (9 *May* 1972)

Electronic absorption and fluorescence of cinchophen, cinchoninic acid and their methyl esters: Biprotonic phototautomerism of the singly protonated species: B. Zalis, A. C. Capomacchia, D. Jackman and S. G. Schulman. (9 *May* 1972)

Locating the more acidic hydroxyl group on dihydroxy compounds. *o*, *o*′-Dihydroxyazo dye metal-ion indicators: Frederick Lindstrom and Ann Edwards Womble. (12 *May* 1972)

Direct polarography in the microdetermination of copper, lead, manganese and calcium in organometallic compounds after oxygen-flask combustion: S. W. Bishara and M. E. Attia. (16 *May* 1972)

Talanta, 1972, Vol. 19, p. i. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Recent Advances in Gas Chromatography: I. I. DOMSKY and J. A. PERRY (Eds.) Dekker, New York, 1971. pp. xi + 414. $19.50.

The book consists of the typescripts of 17 lectures presented at short courses on Gas Chromatography. The reproduction, which is in the modern style, serves to emphasise the origins of the book. Some authors quite clearly were more concerned with delivering a lecture whereas others were also concerned with publication (or providing those attending the lecture with a good paper whilst they spoke of something else). The book is inevitably a pot pourri of discussion and comment on various aspects of GLC such as columns, flow patterns, detectors, computer link-ups, silylation, and applications to the analysis of lipids, pesticides and metabolites. There are also two chapters on gel permeation chromatography.

Most of the chapters contain useful practical information and present it in a straightforward, well-illustrated manner, but overall the rigour demanded of formal papers or books is lacking. It provides a useful survey, and many workers may wish to consult specific chapters, but overall one is left with the impression that, whilst the lectures may have been informative and entertaining, on their translation into book form they should have been expanded and edited.

The Determination of Impurities in Nuclear Grade Sodium Metal: L. Silverman, Pergamon, Oxford, 1971. pp. ix + 143. £3.75, $10.00.

The book appears to be a collection of laboratory procedures for the determination of impurities in sodium metal and also sodium chloride, hydroxide and carbonate. Most emphasis is placed on carbon and oxygen but procedures for the determination of Al, Bi, B, Cd, Ca, Mg, Cs, Cl, Cr, Co, Cu, H, I, Fe, Pb, Li, Nn, Ni, P, K, Si, S and U are also given. There is little theory but the text abounds with practical wisdom, which may be appreciated by many analysts, since the procedures described have a general applicability. The descriptions of procedures are clear and likely pitfalls are pointed out.

Analytical Photochemistry and Photochemical Analysis: J. M. FITZGERALD (Ed.) Dekker, New York, 1971. pp. xiv + 360. $23.50.

The editors hope that the contributions in this volume will bring the developments of photochemistry with analytical implications to the attention of analytical chemists and provide photochemists with a critical survey of useful analytical methods. In view of the rapid growth of photochemistry the work is timely and stimulating. Several useful and unusual determinations are described in a series of reviews by various authors. These deal with lasers in analytical chemistry, actinometry, photochemical titrations and methods for studying the photolysis of polymers and co-ordination compounds, and other related topics.

Analytical Emission Spectroscopy, Vol. 1, Part 1; E. L. GROVE (Ed.), Dekker, New York, 1971. pp. xvi + 401. £12.60.

This is the first part of a projected three part work. Judgment of the whole will have to await the appearance of the whole, but in its own right the first part is most valuable. It contains long articles on the historical development of emission spectroscopy, the origins of atomic spectra, prisms, gratings, prism and grating instruments and spectroradiometric principles. There is little that is new in all this but the spacious accounts of fundamentals are welcome. If the other volumes match this the set will prove an invaluable tome of reference.

ANALYTICAL DATA

An essential but little acclaimed part of scientific research is the measurement of accurate values of the many constants used in the development and application of theory. Development work is usually thought of as interesting and exciting, and careful measurement by established methods as being dull and somehow less praiseworthy. The onlooker is sometimes left with the sneaking suspicion that this attitude sometimes arises because its holder lacks either the patience or the skill necessary for work of the highest accuracy. Be that as it may, it is quite certain that without the consolidation provided by the many careful workers who garner values for constants, theory would not progress very far and would not be nearly so useful as a guide to action. One of the problems of workers in this field is that of publication. Their results are usually of value in several fields of chemistry, but strictly speaking belong to none in particular. A consequence of this is that publication committees are often tempted to suggest submission to some other journal than their own, and authors experience difficulty in finding a medium for publication of their work. One of their difficulties is that journal space is already at a premium, and editors are naturally reluctant to occupy it with details of standard procedures applied to individual problems. We therefore propose to begin a new feature in *Talanta*, to be called "Analytical Data", which will serve for publication of such results with the minimum of background information. Once a pattern of experimentation has been established, a reference to it is all that is necessary to indicate how the work was done. Of course, if there is a new development discovered in the course of such work, that is a different matter, and it can be mentioned in more detail and itself become the reference point for future publications. In this issue we present the first papers in this feature. They are a little longer than we would normally expect, simply in order to set the pattern.

Talanta, 1972, Vol. 19, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Applications of flow microcalorimetry to analytical problems—I. Determination of organophosphorus pesticides by inhibition of cholinesterase enzyme: A. E. Beezer and C. D. Stubbs. (12 *January* 1972)

The acid ionization constants of 2,3-quinoxalinedithiol: J. A. W. Dalziel and A. K. Slawinski. (20 *January* 1972)

The decomposition of hypobromite solutions: N. Velghe and A. Claeys. (26 *January* 1972)

The adsorption of silver on potassium cobalt(II) ferrocyanide: M. Wald, W. Soyka and B. Kaysser. (28 *January* 1972)

Spectrophotometric study of metal pyrogallol complexes: Osmar Nudelman and José A. Catoggio. (1 *February* 1972)

Effect of the addition of quaternary ammonium salts in the extraction of metal-pyrogallol complexes: Osmar Nudelman and José A. Catoggio. (1 *February* 1972)

Detection of nitroprusside by oxidation to nitrite: G. S. Johar. (4 *February* 1972)

The determination of manganese by atomic-fluorescence spectroscopy using a carbon-filament atom-reservoir: L. Ebdon, G. F. Kirkbright and T. S. West. (4 *February* 1972)

Spectrophotometric studies on complexes of some rare-earths with 1-amino-4-hydroxyanthraquinone: A. K. Jain, V. P. Aggarwala, Puran Chand and S. P. Garg. (7 *February* 1972)

Quantitative solvent extraction, spectrophotometric, and gravimetric determination of Cu(II) by metal-exchange in metal–acetylacetonate complexes: M. M. Aly. (7 *February* 1972)

Nomenclature in thermal analysis—II: R. C. Mackenzie, C. J. Keattch, D. Dollimore, J. A. Forrester, A. A. Hodgson and J. P. Redfern. (8 *February* 1972)

Coulometric titration of acids in isopropanol—I. A rapid, direct method for the determination of carbon in steel: B. Metters, B. G. Cooksey and J. M. Ottaway. (9 *February* 1972)

Arsenic(III)–chromium(VI) titration with visual end-point indication: K. Sriramam. (11 *February* 1972)

Fluoride determination with a micro flow-calorimeter: Carl E. Johansson. (15 *February* 1972)

Potentiometric titration of heterocyclic nitrogen bases in non-aqueous media: K. C. Mohan Rao and P. R. Naidu. (15 *February* 1972)

Radiochemical separation of zirconium and hafnium from other radionuclides: Richard B. Hahn. (17 *February* 1972)

Quick, successive determination, in the same sample, of Ca^{2+}, Mg^{2+}, Na^{+}, or other alkali metals, SO$_4^{2-}$ and Cl^{-}: D. Ceauşescu, Ana Sârbu and Maria Aşteleanu. (17 *February* 1972)

Identification de submicroquantités d'iode: N. Gantchev, D. Athanassova and V. Bogdanova. (17 *February* 1972)

Some observations on the redox behaviour of *N*-phenylanthranilic acid indicator in iron(II) titrations: K. Sriramam. (22 *February* 1972)

Application of back-titration of excess EDTA with mercury(II) to the analysis of ores: H. Khalifa and A. I. Atalla. (22 *February* 1972)

The analytical chemistry of melatonin: E. R. Cole and G. Crank. (23 *February* 1972)

Mössbauer investigation of iron-aluminium mixed oxides: L. Korecz, I. Kurucz, G. Menczel, E. Papp-Molnar, E. Pungor and K. Burger. (23 *February* 1972)

Analytical study of the Cu(II)–hydrazine-6-methylpicolinaldehyde system. A new "*in situ*" reaction type: M. Valcarcel and F. Pino. (23 *February* 1972)

Synthesis and ion-exchange properties of ceric antimonate. Separation of Hg^{2+} from Zn^{2+}, Cd^{2+}, **Pb^{2+} and Tl^{+}; Cu^{2+} from Mn^{2+}; Fe^{3+} from Al^{3+}; and Zr^{4+} from Th^{4+};** J. S. Gill and S. N. Tandon. (25 *February* 1972)

The determination of the optimum working range from an auto-analyser calibration curve for colorimetric analysis: D. Whitehead. (28 *February* 1972)

Investigations of dioximes and their metal complexes. A survey of the literature since 1963: Birgitta Egneus. (28 *February* 1972)

Studies on copper(II) sulphide ion-selective electrodes: Gillis Johansson and Kerstin Edström. (1 *March* 1972)

Spectrophotometry of the platinum metals in the ultraviolet region—I. The chloro-complexes of platinum, palladium, rhodium and iridium: Jan Vorlíček and Jan Doležal. (1 *March* 1972)

Talanta, 1972, Vol. 19, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Microtitrimetric determination of uranium in tributylphosphate (30%)–n-dodecane–nitric acid medium in in the presence of excess of iron, magnesium and aluminium: V. Mareška and V. Šraier. (20 *July* 1972)

Spectrophotometric microdetermination of hydroxytriazenes: D. N. Purohit and Kusum C. Goswami. (1 *August* 1972)

2,2′-Dimercaprodiethylsulphide: A potential analytical reagent: A. Corsini and E. Nieboer. (12 *August* 1972)

A mass spectrometric study relating to aspects of the deterioration of polystyrene-based ion-exchangers: G. M. Armitage and S. J. Lyle. (22 *August* 1972)

Coulometric titration of acids in isopropyl alcohol—II. Electrode reactions with lithium chloride and tetraethylammonium bromide as supporting electrolytes: B. G. Cooksey, B. Metters, J. M. Ottaway and D. W. Whymark. (24 *August* 1972).

Calculation of chemical equilibrium concentrations of complexing ligands and metals: A flexible computer programme taking account of uncertainty of formation-constant values: G .A. Cumme. (6 *September*, 1972)

Application of n-(2-acyl-1,3-indandione-1-hydrazone)trialkylammonium iodides-a new group of reagents for the carbonyl group: M. K. Bachlaus and K. L. Menaria. (8 *September* 1972)

Emission-spectrometry detection of metal chelates separated by gas chromatography: Hiroshi Kawaguchi, Takeshi Sakamoto and Atsushi Mizuike. (11 *September* 1972)

Potentiometric determination of stepwise stability constants of zirconium, thorium, and uranium chelates formed with asparagine and glutamine: R. C. Tewari and M. N. Srivastava. (18 *September* 1972)

A study on the theory of action of reversible redox indicators: K. Sriramam. (21 *September* 1972)

Spectrophotometric study of complexes of Zr(IV), Th(IV) and U(VI) nitrates with 1-amino-4-hydroxyanthraquinone: A. K. Jain, V. P. Aggarwala, Puran Chand and S. P. Garg. (21 *September* 1972)

Dichloramine-T as a new oxidimetric titrant in non-aqueous and partially aqueous media: V. Rajasekharan Nair and C. G. Ramachandran Nair. (21 *September* 1972)

Electronic absorption and fluorescence of 9-anthraldehyde and its conjugate cation: John F. Young and Stephen G. Schulman. (28 *September* 1972)

Synthesis and ion-exchange properties of ceric tungstate. Separation of Hg^{2+} from Zn^{2+}, Cd^{2+} and Pb^{2+}; Co^{2+} from Mn^{2+} and Fe^{3+}(and Al^{3+} from Cr^{3+} and Fe^{3+}: J. S. Gill and S. N. Tandon. (3 *October* 1972)

Titrimetric microdetermination of 1,1–diphenyl-2-picryl hydrazal: B. N. Misra, S. K. Gupta and O. C. Saxena. (10 *October* 1972)

Suppression of interference by ammonium bifluoride in the AAS determination of chromium: A. Purushottam, P. P. Naidu and S. S. Lal. (10 *October* 1972)

Application of zone-melting to metal chelate systems—VI. Computer-assisted considerations on the solute distribution in zone melting: Shigeru Maeda, Hiroshi Kobayashi and Keihei Ueno. (11 *October* 1972)

Application of zone melting to metal chelate systems—VII. A new apparatus for zone-melting chromatography: Shigeru Maeda, Hiroshi Kobayashi and Keihei Ueno. (11 *October* 1972)

Reaction of Cu(II) and Cu(I) with 1-isonitroso-(1,2,3,4)-tetrahydrophenazine. Spectrophotometric investigation: Carla Bertoglio Riolo, Teresa Soldi and Giovanni Spini. (12 *October* 1972)

Thin-layer chromatographic method for the separation and determination of papaverine and its oxidation products: G. M. Habashy and Nagy A. Farid. (16 *October* 1972)

Stripping voltammetry with collection at a rotating ring–disc electrode: Dennis C. Johnson and Robert E. Allan. (11 *July* 1972)

Individual microdetermination of chlorine, bromine and iodine in halogenated organic compounds by the oxygen-flask method: Alfy B. Sakla, S. B. Awad and S. A. Abo-Taleb. (29 *August* 1972)

Evaluation of carbon-red atomizer for routine analysis of trace metals by atomic-absorption spectroscopy. Applications to analysis of lubricating oil and crude oil: Gwen Hall, M. P. Bratzel, Jr. and C. L. Chakrabarti. (29 *August* 1972)

Aromatic sulphonate ion-selective electrode membrane using Crystal Violet as ion-exchange site: Nobuhiko Ishibashi, Hitoshi Kohara and Kazuo Horinouchi. (1 *September* 1972)

Development and publication of new methods in kinetic analysis: Harry B. Mark, Jr. (4 *September* 1972)

Determination of uranium content of natural waters by the fission-track technique: Tsuyoshi Takebayashi, Hideki Matsuda and Shunji Umemoto. (4 *September* 1972)

New applications of certain common organic dyes (acriflavine, pyridium, eosin and mercurochrome) in inorganic qualitative analysis. Detection of bromide, bromate, nitrite, thallium(I), lead(II), cadmium(II), copper(II) and iron(III): G. S. Johar. (11 *September* 1972)

A comparative study of some titanium(IV)-based exchangers in a few aqueous and mixed solvent systems: Mohsin Qureshi, Nighat Zehra, Syed Ashfaq Nabi and Virendra Kumar. (12 *September* 1972)

The signal vs. concentration relationships in fluorimetry: R. van Slageren, G. den Boef and V. E. van der Linden. (12 *September* 1972)

Simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroazoles and criteria for their identification—I. Nitroimidazoles and nitropyrazoles-Polarographic determination: Dragica Dumanović and Janka Čirić. (12 *September* 1972)

Chelometric determination of Zn^{2+} or Cd^{2+} in presence of Hg^{2+} by use of thiosalicylic acid as masking agent: M. K. Koul and K. P. Dubey (13 *September* 1972)

Selective extraction and photometric determination of molybdenum in alloy steels: K. Venugopala Rao, K. Ananthanarayana Rao and B. V. Shankar. (13 *September* 1972)

Catalytic hydrogen wave of pre-sodium type formed by selenocystine: V. Voicu and A. Călușaru. (18 *September* 1972)

A general method for the solution of polynomial equations in hydrogen-ion concentration calculations: M. J. D. Brand. (17 *September* 1972)

Gravimetric determination of uranium(VI) with pyridine-2,6-dicarboxylic acid: G. Marangoni S. Degetto and U. Croatto. (27 *September* 1972)

Trace analysis by microwave excitation of sealed samples—I. Preliminary investigations: A. van Sandwijk, P. F. E. van Montfort and J. Agterdenbos. (2 *October* 1972)

Separation of nitroanilines by gas–liquid chromatography: Sabri M. Farrouha, Albertine E. Habboush and Yana A. Barsoum. (17 *October* 1972)

Sulpholane as colour-enhancing and stabilizing agent for silicomolybdic acid: H. Flaschka and J. J. Tice IV. (18 *October* 1972)

The use of hydrazine sulphate as a primary standard for the titrimetric determination of vanadium(V) and chromium(VI): P. V. Krishna Rao and G. Gopala Rao. (19 *October* 1972)

Talanta, 1972, Vol. 19, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Zur Entmischung der Lösungsmittel bei der chromatographischen Trennung—IV. Selektive Sorption der Fließmittel an der Silicagel- und Aluminiumozidsäule sowie an Papierstreigen: JAN MICHAL and GERHARD ACKERMANN. (27 *March* 1972)

Zur Entmischung der Lösungsmittel bei der chromatographischen Trennung—V. Sorption von Fließmitteldämpfen an Cellulose: JAN MICHAL and GERHARD ACKERMANN. (27 *March* 1972)

Synergistic influence of Zn(II) in the extraction–atomic-absorption determination of trace cadmium in waters: K. J. DOOLAN and L. E. SMYTHE. (3 *July* 1972)

Tellurate and periodate solutions as media for paper electrophoresis of carbohydrates: BADER M. I. ALESOFIE and W. J. POPIEL. (3 *July* 1972)

Sulpholane as a solvent for titration of barbiturates and sulpha drugs: TERENCE L. BUXTON and JOSEPH A. CARUSO. (28 *June* 1972)

Spectrophotometric procedure using Rhodamine B for determination of submicrogram quantities of antimony in rocks: MARIAN M. SCHNEPFE. (22 *May* 1972)

Linear crystallization and induction-period studies of the growth of calcium sulphate dihydrate crystals: SUNG-TSEUN LIU and GEORGE H. NANCOLLAS. (20 *June* 1972)

Automatic control of the ion illumination angle on a spark-source mass spectrometer: R. J. CONZEMIUS and H. J. SVEC. (26 *June* 1972)

Relative sensitivity factors for rare earths in spark-source mass spectrometry: R. J. CONZEMIUS and H. J. SVEC. (26 *June* 1972)

A new method for the isolation of methylmercury from biological tissues and its determination at the parts-per-milliard level by gas chromatography: V. ZELENKO and L. KOSTA. (4 *July* 1972)

Spectrophotometric determination of platinum with *o*-phenylenediamine: EDWARD D. GOLLA and GILBERT H. AYRES. (5 *July* 1972)

Fluorimetric method for the determination of uranium in natural waters: ALLAN DANIELSSON and FOLKE INGMAN. (19 *July* 1972)

Formation of Fe(III), La(III) and Ce(III) ferrocyanides—III: ATHOS BELLOMO, DOMENICO DE MARCI and AGATINO CASALE. (25 *July* 1972)

Study on the composition and properties of the ion-association complex of Rhodamine B with silicomolybdic acid with a view to its analytical applications: A. GOLKOWSKA and L. PSZONICKI. (25 *July* 1972)

The application of an oxygen-shielded air-acetylene flame to atomic spectroscopy: R. STEPHENS (26 *July* 1972)

Thiothenoyltrifluoroacetone as extraction and colorimetric reagent for bismuth: K. R. SOLANKE and S. M. KHOPKAR. (26 *July* 1972)

Chromatographic behaviour of 47 metal ions on titanium(IV) arsenate papers: MOHSIN QURESHI, JAGDISH P. RAWAT and MISS VEENZ SHARMA. (26 *July* 1972)

Extraction of molybdenum as molybdenum blue and its application for separation from interfering elements: V. YATIRAJAM and JASWANT RAM. (26 *July* 1972)

Cathodic action of cadmium malate complexes at the dropping mercury electrode: S. C. KHURANA and C. M. GUPTA. (26 *July* 1972)

Formation of silver(I), copper(II) and cadmium(II) ferricyanide—I: ATHOS BELLOMO, AGATINO CASALE and DOMENICO DE MARCO. (27 *July* 1972)

Radio-release determination of nanogram amounts of sulphide: V. KRIVAN, S. PAHLKE and G. TÖLG. (27 *July* 1972)

A new spot test for cyanide ion and cyanogen gas: S. K. TOBIA, Y. A. GAWARGIOUS and M. F. EL-SHAHAT. (27 *July* 1972)

Analytical applications of the reactions of salicylate with uranium(VI) and cobalt(II)-allylamine complex. Micro and semimicro detection of uranium(VI) and salicylate: G. S. JOHAR. (1 *August* 1972)

Application of various electrodes in potentiometric titration of calcium: ADAM HULANICKI and MAREK TROJANOWICZ. (1 *August* 1972)

Use of non-selective reagents in direct thermometry: JÁNOS MARIK, LAJOS BUZÁSI and TAMÁS CSERFALVI. (1 *August* 1972)

Complexometric determination of calcium with arsenazo(III) as metallochromic indicator in a slightly alkaline medium: V. MICHAYLOVA and N. KULEVA. (4 *August* 1972)

Ultramicro atomic-absorption spectroscopy with a tungsten-filament atom reservoir: J. E. CANTLE and T. S. WEST. (4 *August* 1972)

Coulopotentiography: TAITIRO FUJINAGA, SATOSHI OKAZAKI and TAKESHI YAMADA. (4 *August* 1972)

Distribution coefficients of Rb^+ on zirconium phosphate in mixed aqueous–organic media: D. L. MASSART. (4 *August* 1972)

Determination of gold in germanium by neutron-activation analysis: R. GIJBELS. (4 *August* 1972)

Estimation of allyl alcohol by chloramine-T: D. S. MAHADEVAPPA and H. M. K. NAIDU. (4 *August* 1972)

An application of the specific refractive increment in the determination of some inorganic cations. The case of some alkalis and ammonium tetraphenyl-borates: DAISEI YAMAMOTO and TAKASHI NISHIMURA. (9 *August* 1972)

Separation and quantitative determination of the cerium group lanthanides by gas chromatography C. A. BURGETT and J. S. FRITZ. (10 *August* 1972)

Kinetics of selenosemicarbazide oxidation by oxygen in the presence of cupric ions: A. I. BUSEV and K. M. AKHMEDLY. (14 *August* 1972)

Use of furfural thiosemicarbazone for the gravimetric determination of palladium: J. M. CANO PAVON and F. PINO. (14 *August* 1972)

Sulphonated azo-dyes as extractive metallochromic reagents: COLIN WOODWARD and HENRY FREISER. (14 *August* 1972)

Application of indirect methods in analysis by atomic-absorption spectrometry: G. F. KIRKBRIGHT and H. N. JOHNSON. (14 *August* 1972)

Rapid destruction of plant material by use of concentrated nitric acid vapour (vapour phase oxidation): A. D. THOMAS and L. E. SMYTHE. (16 *August* 1972)

Phosphorimetric investigation of the external heavy-atom effect in aqueous solution and its correlation with phosphorescence intensity and quantum efficiency: J. J. AARON, J. J. MOUSA and J. D. WINEFORDNER. (16 *August* 1972)

SIXTH TALANTA MEDAL

In his capacity as Chairman of the Advisory Board, Professor R. **Belcher** (on right) presents the Sixth Talanta Medal to Dr. R. **Přibil** (Czechoslovakia). The award was made for Dr. **Přibil**'s outstanding contribution to analytical chemistry in his development of numerous practical applications of complexometric reagents (see *Talanta*, 1971 **18** *facing* 1175).

Professor A. A. VLČEK, Director of the Polarographic Institute of J. Heyrovský, examines the Medal. Much of Dr. PŘIBIL's work on complexometry has been carried out in the Laboratory of Analytical Chemistry of the Polarographic Institute, Czechoslovak Academy of Sciences.

The presentation was made in Prague during April 1972 at the Polarographic Institute. Amongst the guests were Mrs. Heyrovský (above), wife of the late Professor J. Heyrovský. An Honour Issue of *Talanta* (December 1968) was published to celebrate the seventy-fifth year of Professor Heyrovský.

Talanta, 1972, Vol. 19, pp. i to ii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

Applications of flow microcalorimetry to analytical problems—I. Determination of organophosphorus pesticides by inhibition of cholinesterase enzyme: A. E. BEEZER and C. D. STUBBS. (12 *January* 1972)

The acid ionization constants of 2,3-quinoxalinedithiol: J. A. W. DALZIEL and A. K. SLAWINSKI. (20 *January* 1972)

The decomposition of hypobromite solutions: N. VELGHE and A. CLAEYS. (26 *January* 1972)

The adsorption of silver on potassium cobalt(II) ferrocyanide: M. WALD, W. SOYKA and B. KAYSSER. (28 *January* 1972)

Spectrophotometric study of metal pyrogallol complexes: OSMAR NUDELMAN and JOSÉ A. CATOGGIO. (1 *February* 1972)

Effect of the addition of quaternary ammonium salts in the extraction of metal-pyrogallol complexes: OSMAR NUDELMAN and JOSÉ A. CATOGGIO. (1 *February* 1972)

Detection of nitroprusside by oxidation to nitrite: G. S. JOHAR. (4 *February* 1972)

The determination of manganese by atomic-fluorescence spectroscopy using a carbon-filament atom-reservoir: L. EBDON, G. F. KIRKBRIGHT and T. S. WEST. (4 *February* 1972)

Spectrophotometric studies on complexes of some rare-earths with 1-amino-4-hydroxyanthraquinone: A. K. JAIN, V. P. AGGARWALA, PURAN CHAND and S. P. GARG. (7 *February* 1972)

Quantitative solvent extraction, spectrophotometric, and gravimetric determination of Cu(II) by metal-exchange in metal–acetylacetonate complexes: M. M. ALY. (7 *February* 1972)

Nomenclature in thermal analysis—II: R. C. MACKENZIE, C. J. KEATTCH, D. DOLLIMORE, J. A. FORRESTER, A. A. HODGSON and J. P. REDFERN. (8 *February* 1972)

Coulometric titration of acids in isopropanol—I. A rapid, direct method for the determination of carbon in steel: B. METTERS, B. G. COOKSEY and J. M. OTTAWAY. (9 *February* 1972)

Arsenic(III)–chromium(VI) titration with visual end-point indication: K. SRIRAMAM. (11 *February* 1972)

Fluoride determination with a micro flow-calorimeter: CARL E. JOHANSSON. (15 *February* 1972)

Potentiometric titration of heterocyclic nitrogen bases in non-aqueous media: K. C. MOHAN RAO and P. R. NAIDU. (15 *February* 1972)

Radiochemical separation of zirconium and hafnium from other radionuclides: RICHARD B. HAHN. (17 *February* 1972)

Quick, successive determination, in the same sample, of Ca^{2+}, Mg^{2+}, Na^+, or other alkali metals, SO_4^{2-} and Cl^-: D. CEAUŞESCU, ANA SÂRBU and MARIA AŞTELEANU. (17 *February* 1972)

Identification de submicroquantités d'iode: N. GANTCHEV, D. ATHANASSOVA and V. BOGDANOVA. (17 *February* 1972)

Some observations on the redox behaviour of *N*-phenylanthranilic acid indicator in iron(II) titrations: K. SRIRAMAM. (22 *February* 1972)

Application of back-titration of excess EDTA with mercury(II) to the analysis of ores: H. KHALIFA and A. I. ATALLA. (22 *February* 1972)

The analytical chemistry of melatonin: E. R. COLE and G. CRANK. (23 *February* 1972)

Mössbauer investigation of iron-aluminium mixed oxides: L. KORECZ, I. KURUCZ, G. MENCZEL, E. PAPP-MOLNAR, E. PUNGOR and K. BURGER. (23 *February* 1972)

Analytical study of the Cu(II)–hydrazine-6-methylpicolinaldehyde system. A new "*in situ*" reaction type: M. Valcarcel and F. Pino. (23 *February* 1972)

Synthesis and ion-exchange properties of ceric antimonate. Separation of Hg^{2+} from Zn^{2+}, Cd^{2+}, **Pb^{2+} and Tl^{+}; Cu^{2+} from Mn^{2+}; Fe^{3+} from Al^{3+}; and Zr^{4+} from Th^{4+};** J. S. Gill and S. N. Tandon. (25 *February* 1972)

The determination of the optimum working range from an auto-analyser calibration curve for colorimetric analysis: D. Whitehead. (28 *February* 1972)

Investigations of dioximes and their metal complexes. A survey of the literature since 1963: Birgitta Egneus. (28 *February* 1972)

Studies on copper(II) sulphide ion-selective electrodes: Gillis Johansson and Kerstin Edström. (1 *March* 1972)

Spectrophotometry of the platinum metals in the ultraviolet region—I. The chloro-complexes of platinum, palladium, rhodium and iridium: Jan Vorlíček and Jan Doležal. (1 *March* 1972)

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

The determination of niobium in rocks, ores, and alloys by atomic-absorption spectrophotometry: JOHN HUSLER. (7 *October* 1971)

An improved separation and determination of uranium in sea-water: G. LEUNG, Y. S. KIM and H. ZEITLIN. (12 *October* 1971)

Oxidationen von organischen Substanzen mit Wasserstoffperoxid als Indikatorreaktionen: TIBOR F. A. KISS. (19 *October* 1971)

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous-methanolic solutions: P. C. RAWAT and C. M. GUPTA. (21 *October* 1971)

Foam chromatography. Solid foams as supports in column chromatography: T. BRAUN and A. B. FARAG. (25 *October* 1971)

Some optical studies with the air-acetylene flame: K. M. ALDOUS, R. F. BROWNER, D. CLARK, R. M. DAGNALL and T. S. WEST. (25 *October* 1971)

Molybdänchelonate. Kritische Zusammenfassung mit neuen Ergebnissen: E. LASSNER. (26 *October* 1971)

On the use of simple aliphatic alcohols and acetone in extraction techniques—II. Tridodecylamine-nitric acid-water systems: R. AZZAM, R. SHABANA and A. ALIAN. (26 *October* 1971)

Colorimetric determination of manganese with formaldoxime in some metals and their alloys: RUDOLF PŘIBIL and JIŘÍ ADAM. (29 *October* 1971)

Volumetric determination of xanthate with EDTA: A. L. J. RAO and SURINDER SINGH. (1 *November* 1971)

Extraction study of metal xanthates: A. L. J. RAO and SURINDER SINGH. (1 *November* 1971)

Some considerations on spectral line profiles examined by using microwave-excited electrodeless discharge lamps: D. O. COOKE, R. M. DAGNALL and T. S. WEST. (1 *November* 1971)

Precipitation of nickel *cyclo*heptanedionedioximate from homogeneous solution: J. D. HANNA, SEIN SEIN WIN and O. E. HILEMAN, JR. (2 *November* 1971)

Synthetic, ion-exchange, thermoanalytical and infrared studies on the hydroxide, arsenate, antimonate, molybdate and tungstate of chromium(III): MOHSIN QURESHI, RAJENDRA KUMAR and H. S. RATHORE. (3 *November* 1971)

Determination of subnanogram amounts of chromium in different matrices by flameless atomic-absorption spectroscopy: G. TESSARI and G. TORSI. (3 *November* 1971)

Ammonium hexanitratocerate(IV) as an oxidizing agent—VII. Determination of some carboxylic acids: G. GOPALA RAO, I. SUBRAHMANYAM and B. MADHAVA RAO. (3 *November* 1971)

Some aspects of the Winkler determination of oxygen in water: MICHAEL W. MULLEN and MARK M. JONES. (8 *November* 1971)

Catalysis of the arsenic(III)-potassium bromate reaction—I. The titrimetric determination of arsenic (III) in the presence of osmium tetroxide: D. R. BHATTARAI and J. M. OTTAWAY. (9 *November* 1971)

An indirect method for the determination of aluminium by atomic-absorption spectrometry using an air-acetylene flame: J. M. OTTAWAY, D. T. COKER and B. SINGLETON. (9 *November* 1971)

Titrimetric determination of primary arylamines and nitrites, using an internal indicator system: EUGEN SZEKELY, AMALIA BANDEL and MIRIAM FLITMAN. (11 *November* 1971)

Determination of molybdenum by atomic-absorption spectrophotometry: A. PURUSHOTTAM, P. P. NAIDU and S. S. LAL. (12 *November* 1971)

Voltammetry in dimethylsulphoxide—A review: THOMAS R. KOCH and WILLIAM C. PURDY. (15 *November* 1971)

New tests for detection of the carboxylic acid group in organic compounds with eosin and Mercurochrome: G. S. JOHAR. (15 *November* 1971)

Tropolone as a specific reagent for the determination of vanadium(V): G. H. RIZVI and R. P. SINGH. (16 *November* 1971)

Volume 19, 1972

July–December, Nos. 7–12

SUBJECT INDEX

SUMMARIES FOR CARD INDEXES

Ion-selective chalcogenide electrodes for a number of cations: HIROSHI HIRATA, and KENJI HIGASHIYAMA, *Talanta*, 1972, **19**, 391. (Wireless Research Laboratory, Matsushita Electric Industrial Co., Ltd., Kadoma, Osaka, Japan.)

Summary—Ion-selective chalcogenide disc electrodes have been developed which are responsive to cations such as silver, lead, chromium(III), nickel, cobalt(II), cadmium, zinc, copper(II), and manganese(II) ions. Each was prepared by using the corresponding metal chalcogenide with silver sulphide. An electrode was assembled with both a compacted and a sintered disc. The sintered electrodes were more sensitive and stable than the compacted ones. Response to silver ion was 59·5 mV/pAg, to lead, nickel, cadmium, zinc and copper(II) 29·5 mV/pM and to chromium(III) 20 mV/pM. Cobalt(II) and manganese(II) electrodes had a non-Nernstian response of 25 mV/pM. Both selenides and tellurides can be used for potentiometric determination, but the manganese(II) electrode serves as an analytical tool only when the disc consists of manganese(II) telluride and silver sulphide.

Stalagmometric titrations: TOMIHITO KAMBARA and TOMOE KIBA, *Talanta*, 1972, **19**, 399. (Department of Chemistry, Faculty of Science, Hokkaido University, Saporo, Japan.)

Summary—End-point detection in some precipitation titrations is achieved by measurement of the surface tension between mercury and the solution ("stalagmometric" titration). The drop-time of a polarographic dropping mercury electrode in open circuit is plotted against volume of surface-active titrant added, and shows a break or a peak at the end-point. The stalagmometric titration of sodium tetraphenylborate with Zephiramine (tetradecyldimethylbenzylammonium chloride) was satisfactory and made possible the determination of potassium by back-titration. Potassium was also titrated directly with tetraphenylborate and with calcium dipicrylaminate. Sodium dodecylbenzenesulphonate was titrated directly with Zephiramine and the results were compared with those obtained by the *p*-toluidine method and Epton's method.

Investigation of manganese(III) fluoride for coulometric titration: M. KATOH and T. YOSHIMORI, *Talanta*, 1972, **19**, 407. (Faculty of Engineering, Science University of Tokyo, Shinjuku-ku, Tokyo, Japan.)

Summary—A study has been made of the use of electrogenerated manganese(III), in an electrolyte containing fluoride, for coulometric titration. The addition of fluoride prevented the deposition of manganese dioxide on the anode, and was responsible for increase of the current efficiency and for extension of the feasible range of current density, owing to complex formation between manganese(III) and fluoride. The bonding ratio, the apparent stability constant and the redox potential of the complex were also estimated from the Nernst equation and the current-potential curves.

ИОН-СЕЛЕКТИВНЫЕ ХАЛЬКОГЕНИДНЫЕ ЭЛЕКТРОДЫ ДЛЯ РЯДА КАТИОНОВ:

HIROSHI HIRATA and KENJI HIGASHIYAMA, *Talanta*, 1972, **19**, 391.

Резюме—Разработаны халькогенидные дисковые ион-селективные электроды, чувствительные к таким катионам, как серебро, свинец, хром(III), никель, кобальт(II), кадмий, цинк, медь(II) и марганец(II). Диск изготовлен из соответствующего металлического халькогенида с сернистым серебром. Один электрод собран из компактного и спекшегося дисков. Спекшиеся электроды более чувствительны и устойчивы, чем компактные. Чувствительность к иону серебра была 59,5 mV/pAg, к свинцу, никелю, кадмию, цинку и меди(II) 29,5 mV/pM, а к хрому(III) 20 mV/pM. Электроды из кобальта(II) и марганца(II) имели чувствительность 25 mV/pM (не по Нернсту). Как селениды, так и теллуриды могут применяться для потенциометрического определения, но марганцовый(II) электрод служит для анализа только тогда, когда диск состоит из марганцового(II) теллурида и серебряного сульфида.

СТАЛАГМОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ:

TOMIHITO KAMBARA and TOMOE KIBA, *Talanta*, 1972, **19**, 399.

Резюме—Обнаружение концевой точки титрования некоторых осаждений получается измерением поверхностного натяжения между ртутью и раствором («сталагмометрическое» титрование). Вычерчивается кривая времени падения капель полярографического капельного ртутного электрода в открытой цепи и объема добавленного поверхностно-активного титрующего вещества; кривая показывает перерыв или пик у концевой точки. Сталагмометрическое титрование тетрафенибората с Зефирамином (тетрадецилдиметил-бензиламмоний хлорид) дает удовлетворительные результаты и далает возможным определение калия обратным титрованием. Калий тоже титровался непосредственно тетрафенилборатом и кальцием дипикриламинатом. Натрий додецилбензолсульфонат титровался непосредственно Зефирамином и результаты сравнивались с полученным методом р-толуидиновым и методом Эптона.

ИССЛЕДОВАНИЕ ПРИМЕНИМОСТИ ФТОРИДА МАРГАНЦА(III) В КУЛОНОМЕТРИЧЕСКИХ ТИТРАЦИЯХ:

M. KATOH and T. YOSHIMORI, *Talanta*, 1972, **19**, 407.

Резюме—Изучена применимость электрогенерированного марганца(III), в фторидсодержащем электролите, в кулонометрических титрациях. Присутствие фторида предупреждает осаждение двуокиси марганца на аноде и вызывает повышение выхода по току и расширение применимой области плотности тока, вследствие образования комплекса марганца(III) с фторидом. Отношение связей, кажущаяся константа устоичивости и окислительно-восстановительный потенциал определены с использованием уравнения Нернста и кривых ток-потенциал.

Solvent extraction of anions with metal chelate cations—XVIII. Spectrophotometric determination of maleic acid in the presence of fumaric acid by solvent extraction with tris(1,10-phenanthroline)iron(II) chelate cations: Y. Yamamoto, T. Kumamaru and M. Muranaka, *Talanta*, 1972, **19**, 415. (Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Hiroshima, Japan.)

Summary—A new colorimetric method is proposed for the determination of maleic acid. Among aliphatic dicarboxylic acids tested, maleic acid was found to be selectively extracted into nitrobenzene as the red ion-association complex (λ_{max} 516 nm) formed between the hydrogen maleate anion and the tris(1,10-phenanthroline)iron(II) cation. At least a 32-fold molar excess of tris(1,10-phenanthroline)iron(II) relative to maleic acid is needed and the optimal pH range is 3–5. A linear relationship is obtained over the concentration range 10^{-5}–10^{-4} M maleic acid. The relative standard deviation was 1·0%. The colour intensity of the extract remains constant at room temperature for at least 24 hr. A large amount of fumaric acid, the *trans*-isomer of maleic acid, is not extracted under the same conditions. This makes it possible to determine maleic acid in the presence of fumaric acid.

Studies on interfacial electrochemical phenomena in pigment-vehicle systems: Yoshiaki Ōyabu and Yoshikazu Yasumori, *Talanta*, 1972, **19**, 423. (Nippon Paint Co. Ltd., 246 Kyu-Iketanaka, oaza-Ikeda, Neyagawa, Osaka Japan and Yanagimoto Mfg. Co., Ltd., 28 Joshungamae-cho, Shimotoba, Fushimi-ku, Kyoto, Japan.)

Summary—Sedimentation potentials under a centrifugal field are studied with the disperse system titanium dioxide, alkyd resin and xylene. The relationships between the sedimentation potential and the rotation speed, the distance apart of the electrodes in the cell and the total weight of particles in the disperse system are examined. From the theoretical evaluation of the initial sedimentation potential, the zeta potential of the pigment in the disperse system is calculated. The calculated value was almost coincident with that obtained by the electrophoretic method. As the sedimentation potential is proportional to the total weight of pigment in the space between the electrodes in the cell, the particle-size distribution of pigment can be obtained from the sedimentation potential-time curve. The particle-size distribution in the above-mentioned disperse system was examined with respect to the effect of rotation speed and the pigment content. The modal diameter for the particle-size distribution obtained by this method had almost the same value as that obtained by the electron microscope method. By use of this method for particle-size analysis, the particle-size distribution for particles of diameter <1 μm can be obtained in a short time (*ca.* 10–30 min) and the zeta potential of the particles in the disperse system can be calculated.

СЕЛЕКТИВНАЯ ЭКСТРАКЦИЯ АНИОНОВ МЕТАЛЛИЧЕСКИМИ ХЕЛАТНЫМИ КАТИОНАМИ—XVIII. СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАЛЕИНОВОЙ КИСЛОТЫ В ПРИСУТСТВИИ ФУМАРОВОЙ КИСЛОТЫ СЕЛЕКТИВНОЙ ЭКСТРАКЦИЕЙ ХЕЛАТНЫХ КАТИОНОВ ТРИ (1,10-ФЕНАНТРОЛИН) ЖЕЛЕЗА (II):

Y. YAMAMOTO, T. KUMAMARU and M. MURANAKA, *Talanta*, 1972, **19**, 415.

Резюме—Предлагается новый колорометрический метод для определения малеиновой кислоты. Среди исследованных алифатических дикарбоновых кислот оказалось, что малеиновая кислота селективно экстрагируется в нитробензол как красный ассоциированный ионный комплекс ($\lambda_{\text{макс}}$ 516 нм), образованный анионом малеинового водорода и катионом три (1,10-фенантролин) железа(II). Требуется молярный излишек три (1,10-фенантролин) железа(II) по крайней мере в 32 раза больше чем малеиновой кислоты, оптимальные пределы pH от 3 до 5. Получено линейное соотношение концентраций малеиновой кислоты 10^{-5}–10^{-4} M. Относительное стандартное отклонение было 1,0 %. Интенсивность цвета экстракта остается постоянной при комнатной температуре по крайней мере в течение 24 час. Большое количество фумаровой кислоты, транс-изомера малеиновой кислоты, не экстрагируется при тех же условиях. Это делает возможным определение малеиновой кислоты в присутствии фумаровой кислоты.

ИССЛЕДОВАНИЯ ЭЛЕКТРОХИМИЧЕСКИХ ЯВЛЕНИЙ НА ГРАНИЦЕ РАЗДЕЛА СИСТЕМ ПИГМЕНТ-НОСИТЕЛЬ:

YOSHIAKI ŌYABU and YOSHIKAZU YASUMORI, *Talanta*, 1972, **19**, 423.

Резюме—Изучались потенциалы осаждения в поле центробежных сил дисперсной системы двуокись титана, алкидная смола и ксилол. Исследовались взаимоотношения между потенциалом осаждения и скоростью вращения, расстоянием между электродами в ячейке и общим весом частичек в дисперсной системе. Zeta-потенциал пигмента в дисперсной системе высчитывался из теоретической оценки исходного потенциала осаждения. Высчитанная величина почти совпадала с величиной, полученной методом электрофореза. Так как потенциал осаждения пропорционален общему весу пигмента в расстоянии между электродами в ячейке, то можно было получить распределение частичек пигмента по размерам из кривой потенциал осаждения—время. Распределение частичек по размерам в вышеуказанной дисперсной системе исследовалось в отношении влияния скорости вращения и содержания пигмента. Модальный диаметр для распределения размеров частичек, полученный этим методом имел почти такую же величину, как и полученный при помощи электронного микроскопа. Использование этого метода анализа размеров частичек дает возможность получать распределение частичек по размерам для диаметров частичек <1 μм в течение короткого времени (около 10–30 мин) и высчитывать Zeta-потенциал частичек в дисперсной системе.

Mechanism and analytical aspects of the polarographic maximum wave of tellurium: MUTSUAKI SHINAGAWA, NOBUYUKI YANO and TAKEYUKI KUROSU, *Talanta*, 1972, **19**, 439. (Department of Nuclear Engineering, Faculty of Engineering, Osaka University, Yamadakami, Suita-shi, Osaka, Japan.)

Summary—The polarogram of tellurium(IV) in weakly basic solution has a sharp maximum on the diffusion current plateau. The electrode process causing this maximum has been examined by means of various techniques such as semiconductor catalysis, "block" polarography and ultraviolet irradiation of the dropping mercury electrode. The maximum was found to be caused by the catalytic wave of hydrogen produced by the tellurium deposited on the mercury surface. Part of the tellurium is reduced to hydrogen telluride by nascent hydrogen formed catalytically. The brown mist which usually appears in the vicinity of the surface of the dropping mercury cathode consists of elemental tellurium produced by the decomposition of the hydrogen telluride near the electrode. The sudden decrease in the current maximum at a potential more negative than the peak potential of the maximum is due to desorption of tellurium, caused by movement of mercury.

Separation and determination of ruthenium by evolution with chromium(VI)–condensed phosphoric acid reagent: TOSHIYASU KIBA, KIKUO TERADA, TOMOE KIBA and KAZUO SUZUKI, *Talanta*, 1972, **19**, 451. (Laboratory for analytical Chemistry, Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi-1, Kanazawa, Ishikawa Pref., Japan.)

Summary—Ruthenium in various chemical forms can be evolved as the tetroxide from insoluble matrix materials by heating the sample with chromium(VI)–condensed phosphoric acid reagent (abbreviated as Cr(VI)–CPA). Because of its excellent decomposing power for various solid samples, condensed phosphoric acid is very useful in the chemical analysis of various insoluble materials, and when an oxidizing agent such as potassium dichromate is added in the CPA medium, drastic oxidation proceeds on heating. This method is now extended to the separation of ruthenium from marine sediments. During the reaction with Cr(VI)–CPA ruthenium tetroxide is evolved and collected in an absorbent solution of $6M$ hydrochloric acid and ethanol (1:1), and the ruthenium is then determined spectrophotometrically with thiourea or radiometrically by counting the β- or γ-activity. Osmium, which can be evolved as the tetroxide by the same treatment, can be eliminated beforehand by heating the sample with Ce(IV)–CPA, which removes osmium but not ruthenium. The successive distillations by means of Ce(IV)–CPA and Cr(VI)–CPA give satisfactory results for the separation between osmium and ruthenium. This method might be useful for the separation of ruthenium in geochemical or neutron-activation analysis.

МЕХАНИЗМ И АНАЛИТИЧЕСКИЕ АСПЕКТЫ ПОЛЯРОГРАФИЧЕСКОЙ МАКСИМАЛЬНОЙ ВОЛНЫ ТЕЛЛУРИЯ:

MUTSUAKI SHINAGAWA, NOBUYUKI YANO and TAKEYUKI KUROSU, *Talanta*, 1972, **19**, 439.

Резюме—Полярограмма теллурия(IV) в слабо-основном растворе имеет крутой максимум на части кривой, параллельной оси абсцисс диффузионного потока. Вызывающий этот максимум электродный процесс исследовался различными способами, как напр. полупроводниковым катализом, «блок-полярографией» и ультрафиолетовым облучением капельного ртутного электрода. Найдено, что максимум причиняет каталитическая волна водорода, образующегося теллурием, осажденном на поверхности ртути. Образующийся каталитически водород в момент выделения восстанавливает часть теллурия в теллуристый водород. Коричневый туман, обычно наблюдаемый у поверхности капельного ртутного катода, состоит из элементального теллурия, образующегося вследствие разложения теллуристого водорода у электрода. Внезапное уменьшение максимума потока у потенциала более негативного, чем потенциал максимального пика, происходит благодаря десорбции теллурия, причиняемой движением ртути.

ОТДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ РУТЕНИЯ ПУТЕМ ВЫДЕЛЕНИЯ С РЕАКТИВОМ ХРОМ(VI)-КОНДЕНСИРОВАННАЯ ФОСФОРНАЯ КИСЛОТА:

TOSHIYASU KIBA, KIKUO TERADA, TOMOE KIBA and KAZUO SUZUKI, *Talanta*, **19**, 451.

Резюме—Рутений в различных химических формах может быть выделен как четырёхокись из нерастворимых матричных материлов путем нагрева образца с реактивом хром(VI)-конденсированная фосфорная кислота (сокращ. Cr(VI)-CPA). Благодаря своей превосходной способности разложения различных твердых образцов конденсированная фосфорная кислота очень полезна для химических анализов различных нерастворимых материалов; когда же к среде концентр. фосфр. кислоты добавляется окислитель, как напр. бихромат калия, то при нагревании наступает бурное окисление. Этот метод теперь распространеа на отделение рутения из Морских осаждений. Во время реакции с Cr(VI)-CPA выделяется четырёхокись рутения и собирается в растворе поглотителя—6*M* соляной кислоты и этанола (1:1), затем рутений определяется спектроскопически с тиомочевиной, или радиометрически счетом активности β или γ Осмий, который может выделиться как четырёхокись тем же способом, может быть удален заранее нагревом образца с Cr(IV)-CPA, удаляющем осмий, оставляя рутений. Последующая дистилляция с помощью Ce(IV)-CPA и Cr(VI)-CPA дает удовлетворительное разделение осмия и рутения. Этот метод может быть полезен для отделения рутения в анализах геохимических или активацией нейтронов.

Trace analysis by flameless atomic-absorption spectrometry: Tsugio Takeuchi, Masaaki Yanagisawa and Masami Suzuki, *Talanta*, 1972, **19**, 465. (Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan, and Department of Industrial Chemistry, Faculty of Engineering, Mie University, Kamihama-cho, Tsu-shi, Mie-ken, Japan.)

Summary—The operating conditions of an atomic-absorption system based on flameless atomization have been investigated for trace analysis for Al, Cr, Cu, Fe, Mg and Mn. The sample solution on a tantalum strip was atomized by electrical heating in an inert atmosphere within an absorption chamber. This technique allows the use of small sample sizes and results in a higher sensitivity than that with the conventional flame technique. Some interference effects and applications were investigated.

Spectrophotometric determination of zirconium, uranium, thorium, and rare earths with Arsenazo III after extractions with thenoyltrifluoroacetone and tri-n-octylamine: Hiroshi Onishi and Keiichi Sekine, *Talanta*, 1972, **19**, 473. (Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan.)

Summary—A method is described for the spectrophotometric determination of microgram amounts of zirconium, uranium(VI), thorium and rare earths with Arsenazo III after systematic separation by extraction. First zirconium is extracted into a xylene solution of thenoyltrifluoroacetone (TTA) from about 4*M* hydrochloric acid. Uranium(VI) is then extracted into a xylene solution of tri-n-octylamine from about 4*M* hydrochloric acid. Thorium is next extracted into TTA solution at pH about 1·5, and finally rare earths are extracted into TTA solution at pH about 4·7. Each metal is back-extracted from the organic phase before determination.

Formation and composition of the precipitates of various metal 8-selenoquinoline complexes: Eiichi Sekido, Isamu Fujiwara and Yoshitaka Masuda, *Talanta*, 1972, **19**, 479. (Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan).

Summary—The effect of acidity on the precipitation of various bivalent metal 8-selenoquinoline and 8-mercaptoquinoline complexes has been systematically studied and compared. The metal ions were Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+}. Most of the metal ions, except copper(II) and cobalt(II), precipitate as a 1:2 complex, metal:ligand. However, in hydrochloric acid solution cadmium precipitates as $CdR_2{\cdot}2HCl$ and lead as $PbR_2{\cdot}2HCl$ or $PbR{\cdot}Cl$. Copper(II) is reduced to copper(I) and precipitates as $CuR{\cdot}RH$ at pH above 2·0 and as CuR in strongly acidic solution. Cobalt(II) does not give a precipitate of composition but appears to precipitate as a mixture of $CoR_2{\cdot}RH$ and fixed CoR_2 or as other complexes. The reasons for the formation of the various types of precipitate are considered.

АНАЛИЗ ПРОСЛЕЖИВАНИЕМ ПРИ ПОМОЩИ БЕСПЛАМЕННОЙ СПЕКТРОМЕТРИИ ПОГЛОЩЕНИЯ АТОМОВ:

Tsugio Takeuchi, Masaaki Yanagisawa and Masami Suzuki, *Talanta*, 1972, **19**, 465.

Резюме—Исследовались условия работы с системой атомного поглощения, основанной на беспламенном распылении, для анализа прослеживания Al, Cr, Cu, Fe, Mg, Mn. Раствор образца на танталовой пластинке распылялся электрическим нагревом в инертной атмосфере в абсорбционной камере. Этот метод, давая возможность пользоваться образцами небольших размеров, отличается б’ольшой чувствительностью, чем обычный метод пламенной спектрометрии. Были исследованы применения и некоторые влияния интерференции.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ, УРАНА, ТОРИЯ И РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С ИСПОЛЬЗОВАНИЕМ АРСЕНАЗО III ПОСЛЕ ЭКСТРАГИРОВАНИЯ ТЕНОИЛТРИФТОРАЦЕТОНОМ И ТРИ-Н-ОКТИЛАМИНОМ:

Hiroshi Onishi and Keiichi Sekine, *Talanta*, 1972, **19**, 473.

Резюме—Описан метод спектрофотометрического определения микрограммовых количеств циркония, урана(VI), тория и редкоземельных элементов с использованием Арсеназо III после систематического отделения экстракцией. Сперва экстрагируют цирконий раствором теноилтрифторацетона в ксилоле из приблизительно 4*M* соляной кислоты. Затем экстрагируют уран(VI) ксилоловым раствором три-н-октиламина из приблизительно 4*M* раствора соляной кислоты. Затем экстрагируют торий раствором ТТА при pH 1,5 и конечно редкоземельные элементы раствором ТТА при pH 4,7. Каждый металл титрируют из органической фазы перед определением.

ОБРАЗОВАНИЕ И СОСТАВ ОСАДКОВ РАЗЛИЧНЫХ МЕТАЛЛИЧЕСКИХ 8-СЕЛЕНОХИНОЛИН КОМПЛЕКСОВ:

Eiichi Sekido, Isamu Fujiwara and Yoshitaka Masuda, *Talanta*, 1972, **19**, 479.

Резюме—Проводились систематические исследования и сравнения влияния кислотности на осаждение различных двухвалентных металлов 8-селенохинолинового и 8-меркаптохинолинового комплексов. Ионы металлов были следующие: Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} и Co^{2+}. Большая часть металлических ионов, за исключением меди(II) и кобальта(II) осаждаются в виде комплекса 1:2—металл: лиганд. Однако, в растворе соляной кислоты кадмий осаждается в виде $CdR_2 \cdot 2HCl$, а свинец в виде $PbR_2 \cdot 2HCl$ или $PbR \cdot Cl$. Медь(II) восстанавливается в медь(I) и осаждается в виде $CuR \cdot RH$ при pH выше 2,0 и в виде CuR в крепком кислотном растворе. Кобальт(II) не дает определенного осадка, но осаждается в виде смеси $CoR_2 \cdot RH$ и CoR_2, или в виде других комплексов. Рассматриваются причины образования осадков различных типов.

Determination of phosphorus in hypereutectic aluminium–silicon alloys: KOHICHI MUKAI, *Talanta*, 1972, **19**, 489. (Nippon Light Metal Research Laboratory, Ltd., Kambara, Shizuoka, Japan.)

Summary—A reproducible method is described for determination of small amounts of phosphorus (from 0·0005% to 0·02%) in hypereutectic aluminium–silicon complex alloys. The method permits the separate determination of phosphorus in acid-soluble and acid-insoluble fractions. Phosphomolybdate is extracted with n-butanol–chloroform solvent mixture and back-extracted with a stannous chloride reducing solution. The phosphorus content of a sample cut into small pieces decreases during storage; loss of phosphorus is negligible on acid dissolution under oxidizing conditions.

Enhancement of polarographic reduction currents by a static magnetic field: SHIZUO FUJIWARA and YOSHIO UMEZAWA, *Talanta*, 1972, **19**, 497. (Department of Chemistry, Faculty of Science, University of Tokyo, Hongo 113, Tokyo, Japan.)

Summary—The effect of a magnetic field on d.c. polarographic reduction currents was studied with a static magnetic field applied perpendicularly to the dropping mercury electrode. In the presence of the magnetic field, diffusion or migration currents show a slight but distinct increase. The factors which can influence this effect have been examined experimentally. The effect is interpreted in terms of suppression of transfer of concentration polarization from one drop to the next. It is shown that certain types of maxima are enhanced by application of a magnetic field.

Spectrophotometric determination of water in organic solvents with solvatochromic dyes—II: SADAKATSU KUMOI, HIROSHI KOBAYASHI and KEIHEI UENO, *Talanta*, 1972, **19**, 505. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.)

Summary—The correlation between the absorbance of a merocyanine dye in an organic solvent and the water content of the solvent has been investigated. The merocyanine dyes investigated are 1-methyl-4-[(4-oxo*cyclo*hexa-2,5-dienylidene)-ethylidene]-1,4-dihydropyridine (I), 1-methyl-4-[(2-oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,4-dihydropyridine, 1-methyl-2-[(4-oxo*cyclo*hexa-2,5-dienylidene)-ethylidene]-1,2-dihydropyridine and 1-methyl-2-[(oxo*cyclo*hexa-3,5-dienylidene)-ethylidene]-1,2-dihydropyridine, and the organic solvents are isopropanol, acetone, acetonitrile and pyridine. The possibility of determining a trace amount of water in an organic solvent is demonstrated, and a procedure is proposed for the determination of trace water in pyridine. The sensitivity of the method depends on the solvent, being more sensitive in an aprotic solvent than in a protic one; for example, 0·05 or 0·27 mg of water in 1 ml of acetonitrile or of isopropanol respectively can be detected with **I**, by use of an ordinary spectrophotometer.

ОПРЕДЕЛЕНИЕ ФОСФОРА В ГИПЕРЭВТЕКТИЧЕКИХ СПЛАВАХ АЛЮМИНИЯ И КРЕМНИЯ:

KONICHI MUKAI, *Talanta*, 1972, **19**, 489.

Резюме—Приведен воспроизводимый метод определения небольших количеств фосфора (0,0005% до 0,02%) в сложных гиперэвтектических сплавах алюминия и кремния. Метод позволяет определять фосфор отдельно в растворимых и нерастворимых в кислотах фракциях. Фосфомолибдат экстрагируют смесью н-бутанола и хлороформа и реэкстрагируют с восстанавливающим раствором хлорида олова. Количество фосфора содержанное в пробе разрезанной на маленкие куски уменьшается в течение лежания на складе. Потеря фосфора незначительна после растворения в кислоте при окислительных условиях.

УСИЛЕНИЕ ПОЛЯРОГРАФИЧЕСКИХ ТОКОВ ВОССТАНОВЛЕНИЯ В СТАТИЧЕСКОМ МАГНИТНОМ ПОЛЕ:

SHIZUO FUJIWARA and YOSHIO UMEZAWA, *Talanta*, 1972, **19**, 497.

Резюме—Изучено влияние магнитного поля на постояннотоковые полярографические токи восстановления с использованием статического магнитного поля перпендикулярно к капельному ртутному электрду. В присутствии магнитного поля обнаружено небольшое но ясное усиление диффузионных и миграционных токов. Изучены экспериментально факторы влияющие на этот эффект. Эффект объясняется подавлением переноса концентрационной поляризации от одной капли на другую. Показано что известные типы максимумов усилены действием магнтного поля.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВОДЫ В ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЯХ С СОЛЬВАТОХРОМНЫМИ КРАСИТЕЛЯМИ—II:

SADAKATSU KUMOI, HIROSHI KOBAYASHI and KEIHEI UENO, *Talanta*, 1972, **19**, 505.

Резюме—Исследовалось соотношение между поглощением мероцианиновых красителей в органических растворителях и содержанием воды в последних. Рассматривались следующие мероцианиновые красители: 1-метил-4-[(4-оксоциклогекса-2,5-диенилиден)-этилиден]-1,4-дигидропиридин(I), 1-метил-4-[(2-оксоциклогекса-3,5-диенилиден)-этилиден]-1,4-дигидропиридин, 1-метил-2-[(4-оксоциклогекса-2,5-диенилиден)-этилиден]-1,2-дигидропиридин и 1-метил-2[(2-оксоциклогекса-3,5-диенилиден)-этилиден]-1,2-дигидропиридин; органические растворители были следующие: изопропанол, ацетон, ацетонитрил и пиридин. Демонстрировалась возможность определения следов воды в органическом растворителе и предлагается процедура для определения следов воды в пиридине. Чувствительность метода зависит от растворителя, причем она больше в апротонном растворителе, чем в протонном; напр. 0,05 или 0,27 мгр воды в 1 мл ацетонитрила или изопропанола соответственно могут быть обнаружены I при пользовании обычным спектрофотометром.

Yields of photonuclear reactions for photon-activation analysis with high-energy Bremsstrahlung: Toyoaki Kato and Yoshinaga Oka, *Talanta*, 1972, **19**, 515. (Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan.)

Summary—Experimental reaction yields have been determined for various types of photonuclear reactions, induced in 52 elements by means of Bremsstrahlung irradiation with maximum energies ranging from 30 to 72 MeV, and of detection of the resultant activities with a lithium-drifted germanium detector. From the results obtained, sensitivities in photon-activation analysis were evaluated and the reactivity of high energy photons with nuclei in a wide range of atomic number is discussed. Some nuclear considerations in photon-activation analysis, involving the relative probability of forming each product as a result of the $(\gamma,xnyp)$ reactions are also given.

Solid-liquid extraction as a preconcentration technique in trace element analysis. Extraction of trace impurities from metal chlorides: Atsushi Mizuike, Katsuaki Fukuda and Yoji Ochiai, *Talanta*, 1972, **19**, 527. (Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—Microgram quantities of iron, cobalt, copper, zinc and cadmium are extracted with various aqueous, organic and mixed solvents from chlorides of sodium, potassium, nickel, cadmium, barium and lead prepared by evaporation of aqueous sample solutions. An ultrasonic field accelerates the extraction, and satisfactory trace recoveries and separation factors are achieved in several systems within a reasonable time. The application to a polarographic determination and a two-stage separation technique are also described.

Selective gas-chromatographic detection using an ion-selective electrode-II. Selective detection of fluorine compounds: Tsugio Kojima, Mitsunojo Ichise and Yoshimitsu Seo, *Talanta*, 1972, **19**, 539. (Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.)

Summary—Components in samples are separated on a gas chromatography column using hydrogen as carrier gas. The individual components from the column are passed through a platinum tube heated at 1000°, where they undergo hydrogenolysis, and fluorine compounds are converted into hydrogen fluoride. The hydrogen fluoride is dissolved in a slow stream of an absorption solution, and the fluoride ion concentration in the resulting solution is monitored in a flow-cell with a fluoride ion electrode. The potentiometric output of the cell is converted into a signal, which is proportional to the concentration of fluoride ion, by an antilogarithmic converter, and recorded. The response of the detector to fluorine compounds was about 10000 times that to an equal quantity of other organic compounds, and 5×10^{-11} mole of fluorobenzene could be detected.

РЕЗУЛЬТАТЫ ФОТОЯДЕРНЫХ РЕАКЦИЙ ДЛЯ АНАЛИЗА ФОТОННОЙ АКТИВАЦИИ С ТОРМОЗНЫМ ИЗЛУЧЕНИЕМ БОЛЬШОЙ ЭНЕРГИИ:

Toyoaki Kato and Yoshinaga Oka, *Talanta*, 1972, **19**, 515.

Резюме—Определялись результаты для различных типов экспериментальных фотоядерных реакций, проводимых в 52 элементах посредством тормозного облучения максимальной энергии в пределах от 30 до 72 мегаэлектронвольт, а также обнаружение вызванной активности посредством германиевого детектора с литиевым перемещением. По полученным результатам расценвалась степень чувствительности анализа активацией фотонов и обсуждалась реактивность фотонов большой энергии с ядрами широкого ряда атомных номеров. Приводятся также некоторые соображения по анализу фотонной активацией, связанные с относительной возможностью образования каждого продукта в результате реакций (γ, x, nyp).

ТВЕРДО- И ЖИДКОФАЗНАЯ ЭКСТРАКЦИЯ В КАЧЕСТВЕ МЕТОДА ПРЕДВАРИТЕЛЬНОГО НАКОПЛЕНИЯ ДЛЯ СЛЕДОВОГО ЭЛЕМЕНТАРНОГО АНАЛИЗА. ИЗВЛЕЧЕНИЕ СЛЕДОВЫХ ПРИМЕСЕЙ ИЗ ХЛОРИДОВ МЕТАЛЛОВ:

Atsushi Mizuike, Katsuaki Fukuda and Yoji Ochiai, *Talanta*, 1972, **19**, 527.

Резюме—Микрограммовые количества железа, кобальта, меди, цинка и кадмия извлекают различными водными, органическими и смешанными растворителями из хлоридов натрия, калия, никеля, кадмия, бария и свинца, приготовленных выпариванием водных растворов проб. Ультразвуковое поле поспешает экстракцию и получены удовлетворительные возвраты следов и факторы разделения в ряде систем в относительно коротком времени. Также описано применение метода в полярографическим определении и в двух-стадийном разделении.

СЕЛЕКТИВНОЕ ОБНАРУЖЕНИЕ ГАЗОВОЙ ХРОМАТОГРАФИЕЙ ПРИ ИСПОЛЬЗОВАНИИ ИОНО-СЕЛЕКТИВНОГО ЭЛЕКТРОДА—II. СЕЛЕКТИВНОЕ ОБНАРУЖЕНИЕ СОЕДИНЕНИЙ ФТОРА:

Tsugio Kojima, Mitsunojo Ichise and Yoshimitsu Seo, *Talanta*, 1972, **19**, 539.

Резюме—Компоненты в образцах отделялись в колонне газового хроматографа с водородом в качестве газа-носителя. Отдельные компоненты из колонны пропускались через платиновую трубку, нагретую до 1000°, где они подвергались гидрогенолизу, причем фторовые соединения превращались в фтороводород. Последний растворялся в медленном потоке абсорбирующего раствора; в получившемся растворе концентрация ионов фтора контролировалась в ячейке для потока электродом для ионов фтора. Потенциометрический выход из ячейки превращался посредством антилогарифмического преобразователя в сигнал, пропорциональный концентрации ионов фтора и регистрировался. Чувствительность дететора к соединениям фтора была примерно в 10000 раз больше, чем к такому же количеству других органических соединений; можно было обнаружить также 5×10^{-11} моля фторбензола.

Polarographic studies of cadmium, zinc and manganese(II) iodide complexes in acetonitrile: S. Misumi and M. Aihara, *Talanta*, 1972, **19**, 549. (Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Fukuoka, Japan).

Summary—Cadmium, zinc and manganese(II) iodide complexes have been studied polarographically in acetonitrile and the electrode reactions for these complexes discussed. The overall stability constants of the iodide complexes of these metal ions were evaluated and corrected for the effect of the ion-pairing electrolyte. The values for log β_4 of CdI_4^{2-} and ZnI_4^{2-} are 26·2 and 18·4 respectively and the values found for the Mn(II) iodide complex are log $\beta_1 = 3·5$, log $\beta_2 = 5·6$, log $\beta_3 = 7·8$, log $\beta_4 = 10·0$, log $\beta_5 = 12·2$ and log $\beta_6 = 14·4$. Within certain limits, the wave-height for each complex is proportional to the metal concentration.

Use of ligand buffers for improved selectivity in the polarographic determination of metals. Polarographic determination of zinc in the presence of a large amount of cadmium: Genkichi Nakagawa and Motoharu Tanaka, *Talanta*, 1972, **19**, 559. (Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya, Japan, and Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—The use of ligand buffers composed of a chelating agent and an excess of polarographically inert metal is recommended for the selective polarographic determination of a metal in the presence of a second metal, which has a polarographic wave at a less negative potential than the metal to be determined. Theoretical considerations on the optimum ligand concentration and the optimum composition of the ligand buffer are followed by the determination of zinc in cadmium as an example.

Flow method in high-resolution magnetic resonance: Yutaka Asahi and Eiji Mizuta, *Talanta*, 1972, **19**, 567. (Chemical Research Laboratories, Research and Development Division, Takeda Chemical Ind., Ltd., Oska, Japan.)

Summary—Flow-cells have been designed for following moderately rapid reactions by high-resolution NMR. Labile intermediates such as the yellow thiol form of thiamine and monoethyl carbonate in alkaline solutions were detected by using this device.

ПОЛЯРОГРАФИЧЕСКИЕ ИССЛЕДОВАНИЯ ИОДИСТОВОДОРОДНЫХ КОМПЛЕКСОВ КАДМИЯ, ЦИНКА И МАРГАНЦА(II) В АЦЕТОНИТРИЛЕ:

S. Misumi and M. Aihara, *Talanta*, 1972, **19**, 549.

Резюме—Исследовались полярографическим методом иодистоводородные комплексные соединения кадмия, цинка и марганца(II) в ацетонитриле и обсуждались электродные реакции для этих комплексов. Найдены величины констант общей стабильности иодистоводородных комплексов ионов этих металлов и введены поправки на спаривание ионов электролитом. Величины $\log \beta_4$ CdI_4^{2-} (кадмия) и ZnI_4^{2-} (цинка) равны 26,2 и 18,4 соответственно, а величины для иодистоводородного комплекса Mn(II) (марганца): $\log \beta_1 = 3{,}5$, $\log \beta_2 = 5{,}6$, $\log \beta_3$ 7,8, $\log \beta_4 = 10{,}0$, $\log \beta_5 = 12{,}2$, и $\log \beta_6 = 14{,}4$. В известных границах высота волны для каждого комплекса пропорциональна концентрации металла.

ИСПОЛЬЗОВАНИЕ ЛИГАНДОВЫХ БУФЕРОВ ДЛЯ УЛУЧШЕНИЯ СЕЛЕКТИВНОСТИ В ОПРЕДЕЛЕНИ МЕТАЛЛОВ ПОЛЯРОГРАФИЧЕСКИМ МЕТОДОМ. ПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ЦИНКА В ПРИСУТСТВИИ БОЛЬШИХ КОЛИЧЕСТВ КАДМИЯ:

Genkichi Nakagawa and Motoharu Tanaka, *Talanta*, 1972, **19**, 559.

Резюме—Предложено использование лигандовых буферов представляющих собой хелатообразующий агент и избыток полярографически инертного металла для селективного полярографического определения металла в присутствии другого металла, который имеет полярографическую волну при менее отрицательном потенциале чем определяемый металл. Приведены теоретические обсуждения оптимальной концентрации лиганда и оптимального состава лигандового буфера и разработан метод определения цинка в кадмие в качестве примера.

ПОТОЧНЫЙ МЕТОД МАГНИТНОГО РЕЗОНАНСА ВЫСОКОЙ РАЗРЕШАЮЩЕЙ СПОСОБНОСТИ:

Yutaka Asahi and Eiji Mizuta, *Talanta*, 1972, **19**, 567.

Резюме—Были сконструированы ячейки потоков для прослеживания реакций средней скорости посредством ядерного магнитного резонанса высокой разрешающей способности. Посредством этого прибора были обнаружены неустойчивые промежуточные вещества, как напр. желтая тиоловая форма тиамина и моноэтил карбонат в щелочных растворах.

Application of urease to the precipitation of manganese(II) oxinate from homogeneous solution with urea in the presence of calcium: Seiichiro Hikime, Hitoshi Yoshida, Mitsuhiko Taga and Shigeru Taguchi, *Talanta*, 1972, **19**, 569. (Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Japan.)

Summary—The effect of calcium on precipitation of manganese(II) oxinate from homogeneous solution by means of decomposition of urea with urease was investigated. Manganese was determined satisfactorily in the presence of calcium.

Qualitative analysis of ultraviolet-absorbing substances by use of fluorescent materials: Zenzo Tamura, *Talanta*, 1972, **19**, 573. (Faculty of Pharmaceutical Sciences, University of Tokyo, Tokyo, Japan.)

Summary—Developments of detection techniques of ultraviolet absorbing substances with fluorescent materials are reviewed.

Automatic ion-exchange chromatograph for analysis of alkali and alkaline earth metal mixtures: Shun Araki, Shigetaka Suzuki and Masaaki Yamada, *Talanta*, 1972, **19**, 577. (Department of Industrial Analytical Chemistry, Faculty of Technology, Tokyo Metropolitan University, Setagaya-ku, Tokyo, Japan.)

Summary—A new automatic chromatograph for ultramicro determination of alkali and alkaline earth metals has been developed. It combines a high-sensitivity hydrogen flame-ionization detector with ion-exchange chromatography. Zirconium phosphate was chosen as ion-exchanger.

Spectrophotometric studies on 5,7-dibromo-8-aminoquinoline chelates of some bivalent transition metals: Katsumi Yamamoto and Hiroshi Tabata, *Talanta*, 1972, **19**, 582. (Department of Chemistry, Faculty of Science, Ibaraki University, Mito, Japan.)

Summary—The acid dissociation constant of 5,7-dibromo-8-aminoquinoline and the stability constants of 1:1 chelates of some bivalent transition metals were determined spectrophotometrically in 50% v/v dioxan–water medium at an ionic strength of 0·50 at 25·0 ± 0·1° and compared with those of 8-aminoquinoline. The dissociation constant was found to be $7{\cdot}54 \times 10^{-2}$ and the stability constants (log K_1) were 2·3 (copper), 1·8 (nickel), 1·8 (zinc), 2·2 (cobalt) and 1·6 (cadmium), respectively. The dissociation constants are greater and the stability constants smaller than the corresponding values for 8-aminoquinoline and 8-quinolinol.

ИСПОЛЬЗОВАНИЕ УРЕАЗЫ ДЛЯ ОСАЖДЕНИЯ ОКСИНАТА МАРГАНЦА (II) ИЗ ГОМОГЕННОГО РАСТВОРА МОЧЕВИНОЙ В ПРИСУТСТВИИ КАЛЬЦИЯ:

Seiichiro Hikime, Hitoshi Yoshida, Mitsukiko Taga and Shigeru Taguchi, *Talanta*, 1972, **19**, 569.

Резюме—Изучено влияние кальция на осаждение оксината марганца(II) из гомогенного раствора путем разложения мочевины уреазой. Разработан удовлетворительный метод определения марганца в присутствии кальция.

КАЧЕСТВЕННЫЙ АНАЛИЗ ПОГЛОЩАЮЩИХ В УЛЬТРАФИОЛЕТОВОЙ ОБЛАСТИ СПЕКТРА ВЕЩЕСТВ С ИСПОЛЬЗОВАНИЕМ ФЛУОРЕСЦИРУЮЩИХ МАТЕРИАЛОВ:

Zenzo Tamura, *Talanta*, 1972, **19**, 573.

Резюме—Приведен обзор методов обнаружения поглощающих в ультрафиолетовой области спектратвеществ с использованием флуоресцирующих материалов.

АВТОМАТИЧЕСКИЙ ИОНООБМЕННЫЙ ХРОМАТОГРАФ ДЛЯ АНАЛИЗА СМЕСЕЙ ЩЕЛОЧНЫХ И ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ:

Shun Araki, Shigetaka Suzuki and Masaaki Yamada, *Talanta*, 1972, **19**, 578.

Резюме—Сконструирован новый автоматический хроматограф для ультрамикроопределения щелочных и щелочноземельных металлов. Прибор использует высокочувствительный пламенноионизационный детектор и ионообменную хроматографию. Фосфат циркония использован в качестве ионообменника.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ ХЕЛАТОВ 5,7-ДИБРОМ-8-АМИНОХИНОЛИНА С НЕКОТОРЫМИ ДВУХВАЛЕНТНЫМИ ПЕРЕХОДНЫМИ МЕТАЛЛАМИ:

Katsumi Yamamoto and Hiroshi Tabata, *Talanta*, 1972, **19**, 582.

Резюме—Определены спектрофотометрическим методом константа кислотной диссоциации 5,7-дибром-8-аминохинолина и константы устойчивосчи 1:1 хелатов некоторых двухвалентных переходных металлов в 50 % по объему смеси диоксана и воды при ионной силы 0,50 при 25,0 ± 0,1° и сравнены с константами 8-аминохинолина. Определена константа диссоциации $7,54 \times 10^{-3}$ и константы устойчивости (ly K_I) 2,3 (медь), 1,8 (никель), 1,8 (цинк), 2,2 (кобальт) и 1,6 (кадмий). Константы диссоциации больше, а константы устойчивости меньше чем соответственные величины для 8-аминохинолина и 8-оксихинолина.

Talanta, 1972, Vol. 19, p. ii. Pergamon Press. Printed in Northern Ireland

NOTICES

31st CONGRESS OF THE GROUP FOR ADVANCEMENT OF PHYSICAL METHODS OF ANALYSIS (G.A.M.S.)

This Congress will be held in Paris on 5–9 June 1972 and will be devoted to spectrographic and chromatographic methods of analysis. On the 9th, the proceedings (under the aegis of the Analytical Chemistry Division of the Chemical Society of France) will deal with modern methods of analysis. The meeting will take place in the Salle d'Iéna, 10 Avenue d'Iéna, Paris-16°, and there will be an exhibition of apparatus. Offers of communications should be sent by 15 February 1972 (accompanied by a one-page summary) to

Secrétariat du G.A.M.S. (Congrès)
10 rue du Delta
75-Paris-9°.

Further information may be obtained from the same address.

DECISION, DESIGN AND THE COMPUTER

The Institution of Chemical Engineers is organising a symposium on this topic, in London on 12–14 September 1972. The meeting is the 117th Event of the European Federation and the 5th European Symposium of the Working Party on Routine Calculations and the Use of Computers in Chemical Engineering. The symposium is preceded by a symposium in Paris, on Chemical Engineering at the Service of Mankind, and followed (beginning 18 September) by the International Chemical and Petroleum Engineering Exhibition at Olympia, London. The symposium will deal with Project Evaluation, Computers and Management, Data Banks, Design, Process Models, Parameter Estimation and Data Collection, and On-Line Computers and Plant Operation. Further details may be obtained from

N. T. Shepherd
Institution of Chemical Engineers
16, Belgrave Square, London S.W.1.

TALANTA SCROLL

Professor R. Belcher presenting a special scroll in honour of **Professor C. L. Wilson**'s 60th birthday.

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

A study of the evaporation of gold solutions: D. Buksak and A. Chow. (3 *February* 1972)

A note on successive complexometric determination of thorium and rare earths: Rudolf Přibil and Vladimír Veselý. (2 *March* 1972)

Spectrochemical determination of impurities in telluric acid: B. Zmbova and C. Teofilovski. (7 *March* 1972)

The determination of gallium in an iron-aluminium matrix by solvent extraction and flame-emission spectroscopy: M. S. Cresser and J. Torrent-Castellet. (7 *March* 1972)

Comparative study of analytical properties and applications of picolinaldehyde thiosemicarbazone and selenosemicarbazone: J. M. Cano Pavon and F. Pino. (7 *March* 1972)

The determination of iron, titanium and nickel in Apollo 14 samples by cathode-ray polarography: E. June Maienthal. (9 *March* 1972)

Cation-exchange of metal ions in inorganic solvent-cupferron media: J. Korkisch and M. M. Khater. (13 *March* 1972)

Rapid determination of selenium and tellurium by atomic-absorption spectrophotometry: B. C. Severne and R. R. Brooks. (13 *March* 1972)

Spectrophotometric determination of trace quantities of cobalt(II) with sodium 7-nitroso-8-hydroxyquinoline-5-sulphonate: M. M. Aly. (14 *March* 1972)

Rapid separation and determination of chromium: J. S. Fritz and J. P. Sickafoose. (16 *March* 1972)

Nuclear magnetic resonance analysis of pharmaceuticals—VII The determination of aminophylline in tablets by NMR: J. W. Turczan, R. A. Goldwitz and J. J. Nelson. (17 *March* 1972)

Stability constants of some metal dithizonates: B. W. Budesinsky and M. Sagat. (20 *March* 1972)

Quantitative reflectometry—Principles and scope: David Kealey. (24 *March* 1972)

Simultaneous determination of arsenic, manganese, and selenium in biological materials by neutron-activation analysis: Kaj Heydorn and Else Damsgaard. (27 *March* 1972)

Extraction with long-chain amines—VI Separation of manganese as the $Mn(CN)_6^{4-}$ complex and its complexometric determination in calcareous material: Rudolf Přibil and Jiří Adam. (5 *April* 1972)

Note on the complexation of iron(III) with quinizarin-2-sulphonic acid: B. W. Budesinsky. (5 *April* 1972)

Spectrophotometric determination of strychnine and methyl atropine by extraction with tetrabromophenolphthaleun ethyl ester: Masahiro Tsubouchi, Tadao Sakai, Toshikazu Watake, Kazuhito Kanazawa and Masaya Tanaka. (5 *April* 1972)

Spectrophotometric determination of vanadium with 1,10-phenanthroline: Amal Kanti Bhadra. (7 *April* 1972)

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

NOTICES

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS, 86th ANNUAL MEETING

This meeting will be held on 9–12 October 1972 at Marriott Motor Hotel, Twin Bridges, Washington, D.C. 20001, U.S.A. The topics will be methods of analysis for materials and products important to health and agriculture, *i.e.*, drugs, pesticides, foods, beverages, additives, cosmetics, feeds, fertilisers, microbiological contamination of foods, *etc.* For further information write to L. G. Esminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, U.S.A.

SPECTROSCOPY SOCIETY OF CANADA 19th SPECTROSCOPY SYMPOSIUM AND EXHIBITION

This symposium will be held on 23–25 October 1972 at Le Chateau Champlain Hotel, Montreal, and will deal with optical-emission, atomic-absorption, molecular, X-ray and gamma-ray spectroscopy. The exhibition will cover the complete range of instrumentation in spectroscopy. For further information write to Prof. J. G. Dick, Department of Chemistry, Sir George Williams University, 1435 Drummond Street, Montreal, Quebec, Canada.

INTERNATIONAL SYMPOSIUM ON SELECTIVE ION-SENSITIVE ELECTRODES

A IUPAC symposium on selective ion-sensitive electrodes will be held at the University of Wales Institute of Science and Technology, Cardiff, Wales, on 9–12 April 1972. The programme will be devoted to all aspects of the topic, including development, operation, mechanism and applications. Anyone wishing to present a paper should obtain an application form from the Symposium Editor (Dr. G. J. Moody), Department of Chemistry, UWIST, Cardiff, Wales, U.K. and return it with an abstract of the paper not later than 1 September 1972. Further details and enrolment forms may be obtained from the Symposium Secretary, Mr. D. R. Hub, Organiser of Short Courses, UWIST, Cardiff, Wales, U.K.

SUMMARIES FOR CARD INDEXES

Removal of graphite by oxidation with perchloric acid plus periodic acid. Inapplicability to the spectrophotometric determination of manganese in steel: James A. Gaunt and Harvey Diehl, *Talanta*, 1972, **19**, 1. (Department of Chemistry, Iowa State University, Ames, Iowa, 50010 U.S.A.)

Summary—An attempt has been made to improve the Willard and Greathouse periodate method for the determination of manganese in high-carbon steel and cast iron by oxidizing the graphite with periodic acid in the presence of perchloric acid and phosphoric acid. Graphite is rapidly oxidized at 150° by this mixture but manganese is lost by volatilization as the heptoxide and decomposition of the latter on hot surfaces to manganese dioxide. No way was found for either the quantitative removal and recovery of manganese by volatilization or for quantitative return to the main solution. The spectrophotometric determination of manganese in the supernatant liquid after allowing graphite to settle yields imprecise but not wholly unacceptable results; for the highest accuracy, graphite should be removed along with silica following dehydration of the latter with perchloric acid.

Spectrophotometric determination of calcium in zirconium powder by use of murexide: Herman Gordon and George Norwitz, *Talanta*, 1972, **19**, 7. (Frankford Arsenal, Philadelphia, Pa. 19137, U.S.A.)

Summary—An accurate spectrophotometric method is proposed for the determination of calcium in zirconium powder by use of murexide. A 0·4-g sample is dissolved in hydrofluoric and sulphuric acids, the solution evaporated to fumes of sulphuric acid, and a mercury cathode electrolysis made if more than 0·05% copper or nickel is present. Ammoniacal precipitation in the presence of ammonium chloride separates zirconium and other elements and an aliquot of filtrate is collected, equivalent to 0·2 g of sample. The ammonium salts are destroyed with nitric and hydrochloric acids and the calcium is determined with murexide. The high reagent blank is shown to be due to the reagent grade nitric acid, hydrochloric acid, and ammonium hydroxide.

Microdosage du silicium dans les composés organiques: E. Debal, *Talanta*, 1972, **19**, 15. (Service Central de Microanalyse du Centre National de la Recherche Scientifique, 2, rue Henry Dunant, 94-Thiais, France.)

Summary—Organic silicon compounds are decomposed by sodium peroxide in a Würzschmitt nickel bomb. The silicate obtained is determined spectrophotometrically as silicomolybdate. The sample weight is 2-6 mg. The possible absolute error in the silicon content is 0·3–0·4%.

УДАЛЕНИЕ ГРАФИТА ОКИСЛЕНИЕМ ХЛОРНОЙ И ИОДНОЙ КИСЛОТАМИ. НЕПРИМЕНИМОСТЬ МЕТОДА В СПЕКТРОФОТОМЕТРИЧЕСКОМ ОПРЕДЕЛЕНИИ МАРГАНЦА В СТАЛЯХ:

James A. Gaunt and Harvey Diehl, *Talanta*, 1972, **19**, 1.

Резюме—Сделана попытка улучшать метод Вилларда и Грейтхауза для определения марганца в высокоуглеродных сталях и чугуне окислением графита иодной кислотой в присутствии хлорной и фосфорной кислот. Графит быстро окисляется этой смесью при 150° но марганец теряется улетучиванием в форме гептоксида и разлаганием этого до двуокиси марганца на горячих поверхностях. Не обнаружен метод количественного удаления и регенерации марганца улетучиванием или количественного возврата главному раствору. Спектрофотометрическое определение марганца в всплывающем слое после осаждения графита дает неточные но не весьма неприемлемые результаты. Для получения наилучшей точности надо удалять графит вместе с кремнием, после дегридатации двуокиси кремния хлорной кислотой.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КАЛЬЦИЯ В ПОРОШКОВИДНОМ ЦИРКОНИИ С ИСПОЛЬЗОВАНИЕМ МУРЕКСИДА:

Herman Gordon and George Norwitz, *Talanta*, 1972, 19, 7.

Резюме—Предложен точный спектрофотометрический метод определения кальция в порошковидном цирконии с использованием мурексида. 0,4 г пробы растворяют в фтороводородной и серной кислотах, раствор выпаривают до появления дымов серной кислоты и проводят электролиз с использованием ртутного катода если присутствуют больше чем 0,05 % меди или никеля. Цирконий отделяют от других элементов осаждением аммиаком в присутствии хлорида аммония и собирают аликвотную часть филътрата, соответствующую 0,2 г пробы. Соли аммония разрушают добавлением азотной и соляной кислот, а кальций определяют мурексидом. Показано что высокая слепая проба реагентов вызвана примесами присутствующими в азотной и соляной кислотах и хлориде аммония аналитической чистоты.

ОПРЕДЕЛЕНИЕ МИКРОКОЛИЧЕСТВ КРЕМНИЯ В ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ:

E. Debal, *Talanta*, 1972, **19**, 15.

Резюме—Органические соединения кремния разлагают перекисью натрия в никелевой бомбе Вирцшмитта. Полученный силикат определяют спектрофотометрическим методом в форме силикомолибдата. Для определения берут 2—6 мг пробы. Возможная абсолютная ошибка определения равна 0,3—0,4 % кремния.

Fluorimetric and phosphorimetric characteristics of several vitamins: JEAN-JACQUES AARON and J. D. WINEFORDNER, *Talanta*, 1972, **19**, 21. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—The fluorescence and phosphorescence characteristics of 14 vitamins were evaluated. The existence or absence of fluorescence and phosphorescence was compared with predictions based upon molecular structure. Analytically useful fluorescence signals were obtained for *p*-aminobenzoic acid, folic acid, calciferol, pyridoxine hydrochloride, riboflavine, α-tocopherol and vitamin A, whereas analytically useful phosphorescence signals were obtained for *p*-aminobenzoic acid, folic acid, niacinamide, pyridoxine hydrochloride, and α-tocopherol. All other vitamins either did not fluoresce or phosphoresce or could not be measured, owing to experimental difficulties. The complementary nature of fluorimetry and phosphorimetry is evident in these studies.

Microdetermination of α-amino-acids by spectrophotometric and titrimetric methods: W. I. AWAD, S. NASHED, S. S. M. HASSAN and R. F. ZAKHARY, *Talanta*, 1972, **19**, 31. (Department of Chemistry, University College for Women, Ain Shams University, Cairo, U.A.R. and Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, U.A.R.)

Summary—Micro-methods for spectrophotometric and oxidimetric determination of α-amino-acids are described. They are based on a reaction of the acids with *peri*-naphthindan-2,3,4-trione hydrate at pH 2.5 to give a red precipitate of dihydroxy-*peri*-naphthindenone. The red product is dissolved and measured either spectrophotometrically at 243 nm or titrimetrically by reaction with iodine or *N*-bromosuccinimide. The results obtained by the three methods are concordant, the average recovery being 98%.

Indirect near-infrared spectrophotometric determination of silicate by the 2-amino-4-chlorobenzenethiol method: LOUIS A. TRUDELL and D. F. BOLTZ, *Talanta*, 1972, **19**, 37. (Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.)

Summary—An indirect near-infrared spectrophotometric method for the determination of silicate, based on the absorbance of an equivalent amount of molybdenum-2-amino-4-chlorobenzenethiol complex in chloroform solution, has been developed. The green chloroform solution has an absorbance maximum at 715 nm. The development of the spectrophotometric method for the determination of silicate included a study of a buffer system for the purpose of maintaining the pH within a narrow optimum pH range, complex stability, effect of diverse ions, and conformity to Beer's law. The limit of detection is 0·034 μg of silicon per ml of aqueous heteropoly acid solution.

ФЛУОРИМЕТРИЧЕСКИЕ И ФОСФОРИМЕТРИЧЕСКИЕ ХАРАКТЕРИСТИКИ НЕКОТОРЫХ ВИТАМИНОВ:

JEAN-JACQUES AARON and J. D. WINEFORDNER, *Talanta*, 1972, **19**, 21.

Резюме—Изучены флуориметрические и фосфориметрические характеристики 14 витаминов. Присутствие или отсутствие флуоресценции и фосфоресценции сравнено с предсказаниями на основе молекулярного устройства. Испоьзуемые для анализа флуоресцентные сигналы получены для п-аминобензойной кислоты, фолевой кислоты, кальциферола, хлористоводородного пиридоксина, рибофлавина, α-токоферола и витамина A, а используемые для анализа фосфоресцентные сигналы—для п-аминобензойной кислоты, фолевой кислоты. ниацинамида, хлористоводородного пиридоксина и α-токоферола. В случае всех других витаминов флуоресценция или фосфоресценция не обнаружилась или не удалась измерять вследствие опытных трудностей. Комплементарная природа флуориметрии и фосфориметрии очевидна в этих изучениях.

МИКРООПРЕДЕЛЕНИЕ α-АМИНОКИСЛОТ СПЕКТРОФОТОМЕТРИЧЕСКИМИ И ТИТРОМЕТРИЧЕСКИМИ МЕТОДАМИ:

W. I. AWAD, S. NASHED, S. S. M. HASSAN and R. F. ZAKHARY, *Talanta*, 1972, **19**, 31.

Резюме—Описаны микрометоды спектрофотометрического и титрометрического определения α-аминокислот. Методы основаны на реакции кислот с пери-нафтиндан-2,3,4-трионгидратом при pH 2,5 с образованием красного осадка диокси-пери-нафтинденона. Красный продукт растворяют и измеряют спектрофотометрическим методом при 243 нм или титруют иодом или *N*-имидом бромянтарной кислоты. Эти три метода дают соглашающиеся результаты, средный возврат —98%.

КОСВЕННОЕ ОПРЕДЕЛЕНИЕ СИЛИКАТА СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ В БЛИЗКОЙ ИНФРАКРАСНОЙ ОБЛАСТИ СПЕКТРА С ИСПОЛЬЗОВАНИЕМ 2-АМИНО-4-ХЛОРОТИОФЕНОЛА:

LOUIS A. TRUDELL and D. F. BOLTZ, *Talanta*, 1972, **19**, 37.

Резюме—Разработан косвенный метод определения силиката основывающийся на измерении светопоглощения в близкой инфракрасной области спектра эквивалентного количества комплекса молибдена с 2-амино-4-хлоротиофенолом в растворе хлороформа. Зеленый раствор в хлороформе показывает максимум светопоглощения при 715 нм. Разработка спектрофотометрического метода для определения силиката включила изучение буферной системи для поддержки pH в узких оптимальных пределах, исследование устойчивости комплекса, влияния различных ионов и соблюдения закону Бера. Чувствительность метода 0,034 мкг кремния/мл водного раствора гетерополикислоты.

Studies on potassium chlorate as a primary oxidimetric reagent: C. Radhakrishna Murty and G. Gopala Rao, *Talanta*, 1972, **19**, 45. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Conditions have been established for the use of potassium chlorate as a primary oxidizing agent in the direct titration of vanadium(III), tin(II) and titanium(III) with visual or potentiometric end-points.

A spectrophotometric method for the determination of copper ions and its application to the co-precipitation of copper in the crystallization of sodium chloride: A. Glasner, S. Sarig, D. Weiss and M. Zidon, *Talanta*, 1972, **19**, 51. (Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel.)

Summary—The molar absorptivity of the cyanide complexes $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$, at their isosbestic wavelength (235 nm) is $1{\cdot}13 \times 10^3$ $l.mole^{-1}.mm^{-1}$ and can be used for the quantitative determination of micro-amounts of copper in the ppm range. The determination of 1–10 μg of Cu^{2+} per g of NaCl, or 0·25–2·5 μg/ml, is described in detail. The co-precipitation of copper with NaCl crystallizing from aqueous solutions has been studied by this method.

Ammonium hexanitratocerate(IV) as an oxidizing agent—V. Titrimetric determination of arsenic(III) at room temperature: G. Gopala Rao, K. S. Murty and Muralikrishna Gandikota, *Talanta*, 1972, **19**, 59. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Conditions have been established for the accurate titration of arsenic(III) with ammonium hexanitratocerate(IV) at room temperature in sulphuric, nitric and hydrochloric acid media, using suitable catalysts, and ferroin as indicator.

ИЗУЧЕНИЕ ХЛОРАТА КАЛИЯ В КАЧЕСТВЕ ПЕРВИЧНОГО ОКСИДИМЕТРИЧЕСКОГО РЕАГЕНТА:

C. Radhakrishna Murty and G. Gopala Rao, *Talanta*, 1972, **19**, 45.

Резюме—Определены условия использования хлората калия в качестве первичного оксидиметрического реагента в непосредственном титровании ванадия(III), олова(II) и титана(III) с применением визуального и потенциометрического концев титрования.

СПЕКТРОФОТОМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ МЕДИ И ЕГО ПРИМЕНЕНИЕ В КРИСТАЛЛИЗАЦИИ ХЛОРИДА НАТРИЯ ДЛЯ СООСАЖДЕНИЯ МЕДИ:

A. Glasner, S. Sarig, D. Weisz and M. Zidon, *Talanta*, 1971, **19**, 51.

Резюме—Молярное поглощение цианидных комплексов $(Cu(CN)_3)^{2-}$ и $(Cu(CN)_4)^{2-}$ при их изобестической длины волн (235 нм) составляет 1,13 . 10^3 л.моль$^{-1}$.мин$^{-1}$ и позволяет определять количественно микроколичества меди в области частей на миллион. Подробно описано определение 1–10 мкг Cu^{2+} (г NaCl или 0,25–2,5 мкг) мл. Соосаждение меди с кристаллизирующим из водных растворов хлоридом натрия изучено применяя этот метод.

ГЕКСАНИТРАТОЦЕРАТ(IV) АММОНИЯ В КАЧЕСТВЕ ОКИСЛИТЕЛЯ—V. ТИТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЫШЬЯКА(III) ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ:

G. Gopala, Rao, K. S. Murty and Muralikrishna Gandikota, *Talanta*, 1972, **19**, 59.

Резюме—Определены условия точного титрометрического определения мышьяка(III) гексанитратоцератом(IV) аммония при комнатной температуре в серно-, азотно- и солянокислых средах, с использованием подходящих катализаторов и ферроина в качестве индикатора.

Ammonium hexanitratocerate(IV) as an oxidizing agent—VI. Determination of chromium(III) through oxidation to chromium(VI) at room temperature: G. GOPALA RAO, K. S. MURTY and MURALIKRISHNA GANDIKOTA, *Talanta*, 1972, **19**, 65. (Chemistry Department, Andhra University, Waltair, India.)

Summary—A new method has been developed for the determination of chromium(III), depending on its oxidation to chromium(VI) at room temperature by treatment with 50–100% excess of ammonium hexanitratocerate(IV) in 1·0*M* nitric acid medium. The reaction is complete within 15 min. The unreacted cerium(IV) is titrated potentiometrically with sodium oxalate.

A rapid automatic method for the determination of oxygen in organic substances, using coulometry at controlled potential: K. J. KARRMAN and RONALD KARLSSON, *Talanta*, 1972, **19**, 67. (Department of Analytical Chemistry, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden.)

Summary—An Unterzaucher apparatus for the determination of oxygen in organic compounds is used. The iodine vapour formed in the anhydroiodic acid tube is led by a stream of nitrogen to the cathodic chamber of an electrolysis cell. Here the iodine is reduced at controlled potential at a rotating Pt-electrode. The amount of electricity used is determined by an electronic integrator and read from a digital voltmeter. For weights of samples in the range 0·5–6 mg the standard deviation is about 0·08% oxygen.

Successive complexometric determination of thorium and uranium in sulphuric acid media: M. M. L. KHOSLA and S. P. RAO, *Talanta*, 1972, **19**, 71. (Defence Laboratory, Jodhpur, India and Department of Chemistry, University of Jodhpur, Jodhpur, India.)

Summary—A selective analytical extraction method for rapid successive complexometric determination of thorium(IV) and uranium(VI) in sulphuric acid media is described. The method is based on the extraction of thorium and uranium from sulphuric acid media with *N*-butylaniline or *N*-benzylaniline in chloroform. Both thorium and uranium are selectively and quantitatively extracted in the presence of ascorbic acid and EDTA. Most cations and anions do not interfere. The reduction of uranium(VI) with sodium dithionite at room temperature is rapid and quantitative and superior to that with ascorbic acid, which reduces uranium(VI) in boiling solution. The method is simple, rapid and accurate, and the experimental conditions are not highly critical.

ГЕКСАНИТРАТОЦЕРАТ(IV) АММОНИЯ В КАЧЕСТВЕ ОКИСЛИТЕЛЯ—VI. ОПРЕДЕЛЕНИЕ ХРОМА(III) ПУТЕМ ОКИСЛЕНИЯ ДО ХРОМА(VI) ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ:

G. Gopala Rao, K. S. Murty and Muralikrishna Gandikota, *Talanta*, 1972, **19**, 65.

Резюме—Разработан новый метод определения хрома(III), основчвающийся на окислении до хрома(VI) при комнатной температуре, обработкой с 50–100 % тным избытком гексанитратоцерата(IV) аммония в растворе 1,0*M* азотной кислоты. Реакция окончана в 15 мин. Нереагированный церий(IV) титруют потенциометрическим методом с использованием оксалата натрия.

БЫСТРЫЙ АВТОМАТИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ КИСЛОРОДА В ОРГАНИЧЕСКИХ ВЕЩЕСТВАХ С ПРИМЕНЕНИЕМ МЕТОДА ПОТЕНЦИОСТАТИЧЕСКОЙ КУЛОНОМЕТРИИ:

K. J. Karrman and Ronald Karlsson, *Talanta*, 1972, **19**, 67.

Резюме—Авторы пользуются прибором Унтерцаухера для определения кислорода в органических соедиенениях. Образующиеся в трубке иодистоводородной кислоты пары иода переносятся струей азота в катодный простор электролитической ячейки где иод восстанавливается при контроллированном напряжении на вращающемся платиновом электроде. Употребленное количество электричества определяют электронным интегратором и читают на цифровом вольтметре. Стандартная ошибка для проб 0,5–0,6 г равна около 0,08 % кислорода.

ПОСЛЕДОВАТЕЛЬНОЕ КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТОРИЯ И УРАНА В СЕРНОКИСЛЫХ СРЕДАХ:

M. M. L. Khosla and S. P. Rao, *Talanta*, 1972, **19**, 71.

Резюме—Описан селективный экстрактивный метод быстрого последовательного комплексонометрического определения тория(IV) и урана(VI) в сернокислых средах. Метод основывается на экстракции тория и урана из сернокислих средах *N*-бутиланилином или *N*-бензиланилином в хлороформе. Оба элемента селективно и количественно экстрагируются в присутствии аскорбиновой кислоты и ЭДТА. Большинство катионов и анионов не мешают определению. Восстановление урана(VI) дитионитом натрия при комнатной температуре является быстрым и количественным и лучшим восстановлению аскорбиновой кислотой, которая восстанавливает уран(VI) в кипящих растворах. Метод является несложным, быстрым и точным. а опытные условия не весьма критические.

Titrimetric determination of arsenic(III) with potassium dichromate, using redox indicators: G. Gopala Rao, B. Sarojini and Muralikrishna Gandikota, *Talanta*, 1972, **19**, 74. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Experimental conditions have been established for the accurate direct titrimetric determination of arsenic(III) with potassium dichromate, using ferroin and *N*-phenylanthranilic acid as redox indicators. Interferences have been considered.

The use of triethanolamine in a buffer for the determination of fluoride in calcium and transition metal orthophosphates, using a fluoride-selective electrode: Edward J. Duff and J. L. Stuart, *Talanta*, 1972, **19**, 76. (Department of Preventive Dentistry, Turner Dental School, The University, Manchester, U.K.)

Summary—A method is described for the determination of fluoride in inorganic orthophosphates. Interference by complex-forming metal ions is avoided by the use of a citric acid–triethanolamine buffer, $pH < 7{\cdot}5$.

Determination of phosphorus in coke by the oxygen-flask method: B. P. Kirk and H. C. Wilkinson, *Talanta*, 1972, **19**, 80. (British Coke Research Association, Coke Research Centre, Chesterfield, Derbyshire.)

Summary—Recent developments in the oxygen-flask technique for determination of phosphorus in coke are described. The existing method was modified by use of the recently proposed potassium antimonyl tartrate catalyst for the ascorbic acid reduction of phosphomolybdate.

ТИТРОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЫШЬЯКА(III) ДИХРОМАТОМ КАЛИЯ С ИСПОЛЬЗОВАНИЕМ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНЫХ ИНДИКАТОРОВ:

G. Gopala Rao, B. Sarojini and Muralikrishna Gandikota, *Talanta*, 1972, **19**, 74.

Резюме—Установлены опытные условия для точного непосредственного титрометрического определения мышьяка(III) дихроматом калия, с использованием ферроина и *N*-фенилантраниловой кислоты в качестве окислительно-восстановительных индикаторов. Изучено влияние мешающих веществ.

ИСПОЛЬЗОВАНИЕ БУФЕРА НА ОСНОВЕ ТРИЭТАНОЛАМИНА В ОПРЕДЕЛЕНИИ ФТОРИДИОНА В ОРТОФОСФАТАХ КАЛЬЦИЯ И ПЕРЕХОДНЫХ МЕТАЛЛОВ С ИСПОЛЬЗОВАНИЕМ ЭЛЕКТРОДА СЕЛЕКТИВНОГО ДЛЯ ФТОРИДИОНОВ:

Edward J. Duff and J. L. Stuart, *Talanta*, 1972, **19**, 76.

Резюме—Описан метод определения фторида в неорганических ортофосфатах. Влияние комплексообразующих ионов металлов избегнуто использованием буфера для $pH > 7.5$, состоящегося из лимонной кислоты и триэтеноламина.

ОПРЕДЕЛЕНИЕ ФОСФОРА В КОКСЕ МЕТОДОМ СОЖЖЕНИЯ В КОЛБЕ, НАПОЛНЕННОЙ КИСЛОРОДОМ:

B. P. Kirk and H. C. Wilkinson, *Talanta*, 1972, **19**, 80.

Резюме—Описаны успехи полученные в определении фосфора в коксе методом сожжения в колбе, наполненной кислородом. Обыкновенный метод изменен использованием недавно предложенного виннокислого антимонил-калия в качестве катализатора для восстановления фосфомолибдата аскорбиновой кислотой.

Spectrophotometric study of the determination of copper with ammonium 1-pyrrolidinecarbodithioate: R. W. LOOYENGA and D. F. BOLTZ, *Talanta*, 1972, **19**, 82. (Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.)

Summary—A new spectrophotometric method for the determination of traces of copper has been developed. The method is based on the formation of a stable 1:2 complex of copper(II) and 1-pyrrolidinecarbodithioate and the isolation of this complex by extraction into chloroform. The absorbance is measured at either 269 nm or 435 nm. The detection limit is 0.03 μg of copper per ml for absorbance measurements at 435 nm.

Stabilities of some cyclopentadienide metal complexes: B. W. BUDESINSKY and J. SVEC, *Talanta*, 1972, **19**, 87. (Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.)

Summary—The composition and stabilities of hydrogen, manganese(II), iron(II), cobalt(II), nickel(II) and palladium(II) complexes with cyclopentadienide were investigated spectrophotometrically in aqueous and dimethylformamide solutions. Corresponding effective and overall stability constants were determined.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ИЗУЧЕНИЕ ОПРЕДЕЛЕНИЯ МЕДИ С ИСПОЛЬЗОВАНИЕМ I—ПИРРОЛИДИНКАРБОДИТИОАТА АММОНИЯ:

R. W. Looyenga and D. F. Boltz, *Talanta*, 1972, **19**, 82.

Резюме—Разработан новый спектрофотометрический метод определения следовых количеств меди. Метод основывается на образовании устойчивого комплекса 1:2 меди(II) с 1-пирролидинкарбодитиоатом аммония и выделении этого комплекса извлечением с хлороформом. Светопоглощение измеряют при 269 или 435 нм. Чувствительность метода 0,03 мкг меди/мл в случае измерения светопоглощения при 435 нм.

УСТОЙЧИВОСТЬ НЕКОТОРЫХ КОМПЛЕКСОВ МЕТАЛЛОВ С ЦИКЛОПЕНТАДИЕНОМ:

B. W. Budesinsky and J. Svec, *Talanta* 1972, **19**, 87.

Резюме—Исследованы спектрофотометрическим методом состав и устойчивость комплексов водорода, марганца(II), железа(II), кобальта(II), никеля(II) и палладия(II) с циклопентадиеном в водных растворах и растворах в диметилформамиде. Определены эффективные и общие константы устойчивости.

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Recent Advances in the Analytical Chemistry of the Noble Metals: F. E. BEAMISH and J. C. VAN LOON. Pergamon, Oxford, 1972. Pp. xvi + 511. £14.00.

Readers of this journal will be familiar with the scope, detail and critical standards of this book since several of the chapters are based on Talanta Reviews. The work updates the earlier *Analytical Chemistry of the Noble Metals* and provides testimony to the activity in this field. It deals with methods of separation and determinations based on AAS, neutron-activation, spectrochemical, XRF, electrometric, spectrophotometric, gravimetric, and titrimetric methods. With over 1600 references and lots of working procedures and summarizing tables it is destined to be a standard work.

***N*-Benzoylphenylhydroxylamine and its analogues:** A. K. MAJUMDAR. Pergamon, Oxford, 1972. Pp. x + 210. £7.00.

One of the virtues of the international series of Monographs in Analytical Chemistry, of which this is the 49th member, has been the introduction of books which provide an extended review of a novel or interesting aspect of the subject. Hitherto the volumes have been cheap enough to enable the interested analyst to acquire a shelf full of such volumes. This book is in the tradition of the series, but the price is going to limit its circulation. *N*-Benzoylphenylhydroxylamine (even if it doesn't rate as an "all-time great" alongside 1,10-phenanthroline, DMG and EDTA) and it is useful to have its scope clearly delineated by one who has been closely associated with its analytical application for over a decade.

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

PAPERS RECEIVED

A study of the evaporation of gold solutions: D. BUKSAK and A. CHOW. (3 *February* 1972)

A note on successive complexometric determination of thorium and rare earths: RUDOLF PŘIBIL and VLADIMÍR VESELÝ. (2 *March* 1972)

Spectrochemical determination of impurities in telluric acid: B. ZMBOVA and C. TEOFILOVSKI. (7 *March* 1972)

The determination of gallium in an iron-aluminium matrix by solvent extraction and flame-emission spectroscopy: M. S. CRESSER and J. TORRENT-CASTELLET. (7 *March* 1972)

Comparative study of analytical properties and applications of picolinaldehyde thiosemicarbazone and selenosemicarbazone: J. M. CANO PAVON and F. PINO. (7 *March* 1972)

The determination of iron, titanium and nickel in Apollo 14 samples by cathode-ray polarography: E. JUNE MAIENTHAL. (9 *March* 1972)

Cation-exchange of metal ions in inorganic solvent-cupferron media: J. KORKISCH and M. M. KHATER. (13 *March* 1972)

Rapid determination of selenium and tellurium by atomic-absorption spectrophotometry: B. C. SEVERNE and R. R. BROOKS. (13 *March* 1972)

Spectrophotometric determination of trace quantities of cobalt(II) with sodium 7-nitroso-8-hydroxyquinoline-5-sulphonate: M. M. ALY. (14 *March* 1972)

Rapid separation and determination of chromium: J. S. FRITZ and J. P. SICKAFOOSE. (16 *March* 1972)

Nuclear magnetic resonance analysis of pharmaceuticals—VII The determination of aminophylline in tablets by NMR: J. W. TURCZAN, R. A. GOLDWITZ and J. J. NELSON. (17 *March* 1972)

Stability constants of some metal dithizonates: B. W. BUDESINSKY and M. SAGAT. (20 *March* 1972)

Quantitative reflectometry—Principles and scope: DAVID KEALEY. (24 *March* 1972)

Simultaneous determination of arsenic, manganese, and selenium in biological materials by neutron-activation analysis: KAJ HEYDORN and ELSE DAMSGAARD. (27 *March* 1972)

Extraction with long-chain amines—VI Separation of manganese as the $Mn(CN)_6^{4-}$ complex and its complexometric determination in calcareous material: RUDOLF PŘIBIL and JIŘÍ ADAM. (5 *April* 1972)

Note on the complexation of iron(III) with quinizarin-2-sulphonic acid: B. W. BUDESINSKY. (5 *April* 1972)

Spectrophotometric determination of strychnine and methyl atropine by extraction with tetrabromophenolphthaleun ethyl ester: MASAHIRO TSUBOUCHI, TADAO SAKAI, TOSHIKAZU WATAKE, KAZUHITO KANAZAWA and MASAYA TANAKA. (5 *April* 1972)

Spectrophotometric determination of vanadium with 1,10-phenanthroline: AMAL KANTI BHADRA. (7 *April* 1972)

Talanta, 1972, Vol. 19, p. iii. Pergamon Press. Printed in Northern Ireland

NOTICES

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS, 86th ANNUAL MEETING

This meeting will be held on 9–12 October 1972 at Marriott Motor Hotel, Twin Bridges, Washington, D.C. 20001, U.S.A. The topics will be methods of analysis for materials and products important to health and agriculture, *i.e.*, drugs, pesticides, foods, beverages, additives, cosmetics, feeds, fertilisers, microbiological contamination of foods, *etc.* For further information write to L. G. Esminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, U.S.A.

SPECTROSCOPY SOCIETY OF CANADA 19th SPECTROSCOPY SYMPOSIUM AND EXHIBITION

This symposium will be held on 23–25 October 1972 at Le Chateau Champlain Hotel, Montreal, and will deal with optical-emission, atomic-absorption, molecular, X-ray and gamma-ray spectroscopy. The exhibition will cover the complete range of instrumentation in spectroscopy. For further information write to Prof. J. G. Dick, Department of Chemistry, Sir George Williams University, 1435 Drummond Street, Montreal, Quebec, Canada.

INTERNATIONAL SYMPOSIUM ON SELECTIVE ION-SENSITIVE ELECTRODES

A IUPAC symposium on selective ion-sensitive electrodes will be held at the University of Wales Institute of Science and Technology, Cardiff, Wales, on 9–12 April 1972. The programme will be devoted to all aspects of the topic, including development, operation, mechanism and applications. Anyone wishing to present a paper should obtain an application form from the Symposium Editor (Dr. G. J. Moody), Department of Chemistry, UWIST, Cardiff, Wales, U.K. and return it with an abstract of the paper not later than 1 September 1972. Further details and enrolment forms may be obtained from the Symposium Secretary, Mr. D. R. Hub, Organiser of Short Courses, UWIST, Cardiff, Wales, U.K.

PROFESSOR C. L. WILSON

CECIL LEEBURN WILSON was born in Co. Londonderry on 11 May 1912. He attended Rainey Endowed School at Magherafelt and later studied chemistry at Queen's University, Belfast, where he graduated with a first class honours B.Sc. in 1932. The following year he took his M.Sc. at Queen's. A Musgrave research scholarship took him to the University of Glasgow in 1933 where he obtained a Ph.D. in 1936. In 1935 however, he was appointed to an Assistant Lectureship in Chemistry at the Sir John Cass College, London. During the war he was released from there to work with the Armaments Research Department, Ministry of Supply, where he stayed for the years 1940–1944. He then resumed work at the Cass College but in 1946 returned to his Alma Mater in Belfast and has stayed there ever since. Appointed originally as a Lecturer, he became a Reader in 1950. In 1953 he took his D.Sc. at Queen's and in 1958 was appointed to a personal chair in Analytical Chemistry, the first of these ever created in the United Kingdom. The personal chair was converted into an established chair in Inorganic and Analytical Chemistry, which in turn has been split into separate chairs, Cecil Wilson retaining the chair of Analytical Chemistry.

It was in Glasgow that Cecil Wilson's interests were first turned towards microchemistry, and as early as 1935 he designed and introduced an undergraduate course in this subject in Belfast. His first book, entitled "An Introduction to Microchemical Methods" was published in 1938. During the war he had to do mainly analytical—often microanalytical— work for the Ministry of Supply, and from this time his interest in analytical chemistry became dominating. In co-authorship with Professor R. Belcher he published a book on Inorganic Microanalysis in 1946, 2nd edition 1957, and a similar co-operation produced various editions of "New Methods of Analytical Chemistry". Although his interests in teaching and research in Analytical Chemistry were always predominant, he found time and energy to keep up with Inorganic and Physical Chemistry. At the request of his old Professor at Queen's, Dr Stewart, he collaborated on the 7th edition of "Recent Advances in Inorganic and Physical Chemistry", the 6th edition of which had been completely destroyed before publication, by fire during the London blitz. The book, published under the names of Stewart and Wilson, appeared in 1941. Later, with his colleague Barnett at Cass College, he produced the well-known textbook of Barnett and Wilson: Inorganic Chemistry.

As an Editor, Professor Wilson served the community of Analytical Chemists in many ways. He was elected to the editorial board of *Microchimica Acta* in 1949, and has served on it ever since; between 1955 and 1962 he also acted as regional editor for papers written in English. When *Talanta* was established in 1958 as a new journal for Analytical Chemistry, Cecil Wilson became its first Editor-in-Chief, acting as such up to 1964, and since then acting as consulting editor. In 1959, in collaboration with his brother, D. W. Wilson, he became editor of the series "Comprehensive Analytical Chemistry" and since its foundation in 1967 he has served on the editorial board of *Analytical Letters*.

The Society for Analytical Chemistry called upon Cecil Wilson's services on several occasions. He has served on the Council three times since 1951. He was a founding member of the Microchemical Group, and acted as Chairman for the same group in

1951–52. He is a Fellow of the Royal Institute of Chemistry and has acted for years as the Chairman of the Northern Ireland section. His growing international reputation led to Honorary Membership of the Austrian Microchemical Society in 1955, and he was elected to Membership of the Royal Irish Academy in 1966.

Although his duties as Professor and Head of Department leave little time for non-professional activities, he manages to find time to act as Document Examiner for the Ministry of Home Affairs of Northern Ireland, appearing frequently as expert witness in court proceedings. He has held this appointment since 1953. He also served for six years on the Northern Ireland regional Committee of the Independent Television Authority.

Cecil Wilson started to do research in microchemistry, microscopy, micro- and ultramicroanalysis, but his interests widened when he had the opportunity of building up his own Department and research school at Queen's. About 100 papers and more than 30 research students bear witness to these activities.

While congratulating him on his sixtieth birthday, we wish Cecil Wilson further successes in his wide range of activities.

GYULA SVEHLA

Talanta, 1972, Vol. 19, pp. iii to iv. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Nuclear Analytical Chemistry I (Introduction to Nuclear Analytical Chemistry): J. Tölgyessy, Š. Varga, and V. Kriváň. University Park Press, Baltimore, and Publishing House of the Slovak Academy of Sciences, Bratislava (Czechoslovakia), 1971. Pp. 270.

With this book the authors start a five-volume series scheduled to appear in a relatively short period. The division of the rich and constantly developing material among the five books seems to be quite natural: I—Introduction; II—Radioactive indicators (isotope dilution, radioreagents, radiometric titration, radio-release); III—Radiochemical and activation analysis (environmental analysis); IV—Interaction of nuclear radiation with matter; V—Tables, Nomograms, Schemes. The first volume covers both the fundamentals of nucleonics (types of radiation, radioactivity laws, detection, safety, sample preparation) and some chapters interesting for the analyst (criteria for the choice of suitable radioisotopes in the tracer method, behaviour of radioactive substances in trace amounts, selection of an isotope indicator).

The authors are well qualified for their task because each of them had made several important contributions to the field of nuclear analytical chemistry (radiometric titration, radio-release method *etc*) and moreover Prof. Tölgyessy is author of several more specialized books dealing with certain aspects of nuclear analytical chemistry. The present introduction to the whole series is well balanced, quite readable and gives the newcomer to the practical use of nuclear phenomena in analytical chemistry all the information he would otherwise have to look for in several separate books.

The "seams" between separate chapters (written mostly by one, sometimes by two of the authors are almost invisible. Errors and shortcomings are relatively rare (the authors do not mention ways of resolving a decay curve of two independent radioisotopes by other means than graphically). As a whole the first volume of the series is a promise that the whole work will be a very useful systematic and comprehensive presentation of nuclear methods in analytical chemistry.

Mössbauer Spectroscopy: N. N. Greenwood and T. C. Gibb, Chapman & Hall, London, 1971. Pp. xii + 659. £12.00.

This is a standard work for chemists, on the most recent addition to the range of spectroscopic techniques now available to them. After a historical introduction to the Mössbauer Effect the book gives a concise account of the more recent experimental techniques which have been developed for the study of the iron and tin resonance absorption. The hyperfine structures in the spectra so obtained are detailed in the following chapter together with explanations of the physical effect and processes responsible for their observation. There follows a large section dealing with the absorptions due to ^{57}Fe in a variety of compounds. Of particular interest is the section devoted to compounds of biological origin such as the blood pigments. A similar detailed discussion is provided for the resonances due to ^{119}Sn and the book closes with a survey of the applications of the Mössbauer effect to other elements in the periodic table. Appendices listing the nuclear data for Mössbauer transitions and the relative intensities of hyperfine lines are provided.

Field Ionisation Mass Spectrometry: Hans-D. Beckey. Pergamon, Oxford, 1971. Pp. xvi + 344. £9.50.

Field ionization is one of the most recent techniques which have been added to the armoury of the mass spectrometrist for the qualitative analysis of organic compounds. The book gives an account of the theoretical implications of this technique and of the construction of field ionization sources. The application of the field ionization methods to physico-chemical problems is outlined and there is a full description of the use of field-ionization mass-spectrometry in the examination of organic structures. The newer technique of field desorption is also described together with other effects which are observed in high potential gradients. The book is written by the originator of the method.

Liquid Scintillation Counting, Vol. I: ed. A. Dyer. Heydon, London, 1971. Pp. vii + 133. £4.60.

This book is a record of an International Symposium on Liquid Scintillation Counting held at the University of Salford on 21–22 September 1970. The papers presented covered a wide field from the physics and physical chemistry of the scintillation process to biochemical studies using tracers and to the applications of computers to the processing of scintillation data.

Activation Analysis in Geochemistry and Cosmochemistry: ed. Arild O. Brunfelt and Eiliv Steinnes. Scandinavian University Books, Oslo, 1971, Pp. 468. Nkr 144.0

This is an account of the proceedings of a meeting of the Nato Advanced Study Institute held at Kjeller, Norway, 7–12 September 1970. There were ten sessions describing the applications of the many activation techniques to the study of rock and fossil specimens. Considerable emphasis was given in several contributions to the examination of samples of extra-terrestrial origin.

Chemical Analysis of Additives in Plastics: T. R. Crompton. Pergamon, Oxford, 1971. Pp. xi + 162. £7.00.

The term "plastics" in the title of this book is slightly misleading as the analysis of rubber additives is also included. The identification and determination of antioxidants, ultraviolet stabilizers, peroxides, plasticizers, some residual monomers and other additives are described. Column, paper, thin-layer and gas–liquid chromatography together with various forms of spectroscopy, form the backbone of the analytical techniques employed. The book is intended to fill a gap in the literature on the analytical chemistry of polymers and should be of particular value to chemists in the polymer manufacturing and fabrication industries. The half-tone diagrams are poor in quality and add very little to the substance of the text. There are 330 references.

Analytical Chemistry of Molybdenum and Tungsten: W. T. Elwell and D. F. Wood, Pergamon, Oxford, 1971. Pp. xi +277. £8.00.

This book, Volume 47 in the "International Series of Monographs in Analytical Chemistry", is a comprehensive treatment of the analytical chemistry of molybdenum and tungsten from a practical viewpoint. There is virtually no comparison or contrast made between the elements, and the discussions of their respective methods of determination run parallel throughout the book. Each analytical method is dealt with in a separate chapter, the methods comprising the so-called classical methods as well as electrical methods (polarography, amperometry, and coulometry), emission spectroscopy, atomic absorption, X-ray spectroscopy, radiochemistry and mass spectrometry. There are introductory chapters dealing with the physical and chemical properties, sampling, decomposition, qualitative detection, and separations, as well as a short chapter on miscellaneous methods and a final chapter on the determination of impurities and alloying elements. Each chapter comprises a short introductory critique of the method under consideration, followed by a discussion in depth of the particular method and the practical procedure for a variety of sample types, including iron, steel, ores and biological materials. The excellent presentation of the book, the succinct style and care over detail (*e.g.*, giving the systematic names of chromogens as well as the trivial names) make the book both easy to read and to understand.

Proceedings of the 2nd Conference on Applied Physical Chemistry, Veszprém, Hungary, 1971: edited by I. Buzás. Akadémiai Kiadó, Budapest, 1971. Two volumes, pp. 759 and 738. £12.00 the set.

The practice of requiring authors to submit the texts of their papers before a conference begins has led to the laudable result that the proceedings can be published soon enough to retain their value as a reflection of the current state of development of the topic. The editors who achieve this feat of rapid publication are always to be congratulated on their dedication and enthusiasm. These two volumes, which include the proceedings of the second Electroanalytical Symposium and the sixth Symposium on Oscillometry could well be required reading for chemistry students, to let them see the extraordinary breadth of application of chemical principles in technology today.

Ekstraktsiya neorganicheskikh soedinenii: V. V. Bagreev, Yu. A. Zolotov, N. A. Kurilina and G. F. Kalinina, Izdat. "Nauka", Moscow, 1971. Two Volumes, 1945–1962 and 1963–1967. Vol. 1, pp. 328, 2R.40Kop. Vol. 2, pp. 336, 2R.13Kop.

The two volumes represent an enormous amount of work on the part of the authors, who have compiled a bibliography of solvent extraction methods from 1945 to 1967, arranging the entries in alphabetical order of first author's name, and classifying the material by subject. A comprehensive index makes it easy to find an author or a subject in the main text. Each entry gives the authors' names, title of the paper, the reference, and a Russian translation of the title. The subject indexes alone come to over 100 pages.

Fundamental Chemical Equilibria: Nonionic—Ionic: Kelso B. Morris, Gordon and Breach, New York, 1971. Pp. x + 110. $12.50.

The cover says that this book is a modern treatment of chemical equilibria, and it is therefore rather a surprise to find no mention of Ringbom's development of conditional constants and their applications, nor of graphical methods of problem solving and information display. There are many existing texts on the topic that would appear to offer more value for money. It is a pity that "tautomerism" double arrows (⇄) and "equilibrium" signs (⇌) have been used more or less indiscriminately.

PROFESSOR C. L. WILSON

CECIL LEEBURN WILSON was born in Co. Londonderry on 11 May 1912. He attended Rainey Endowed School at Magherafelt and later studied chemistry at Queen's University, Belfast, where he graduated with a first class honours B.Sc. in 1932. The following year he took his M.Sc. at Queen's. A Musgrave research scholarship took him to the University of Glasgow in 1933 where he obtained a Ph.D. in 1936. In 1935 however, he was appointed to an Assistant Lectureship in Chemistry at the Sir John Cass College, London. During the war he was released from there to work with the Armaments Research Department, Ministry of Supply, where he stayed for the years 1940–1944. He then resumed work at the Cass College but in 1946 returned to his Alma Mater in Belfast and has stayed there ever since. Appointed originally as a Lecturer, he became a Reader in 1950. In 1953 he took his D.Sc. at Queen's and in 1958 was appointed to a personal chair in Analytical Chemistry, the first of these ever created in the United Kingdom. The personal chair was converted into an established chair in Inorganic and Analytical Chemistry, which in turn has been split into separate chairs, Cecil Wilson retaining the chair of Analytical Chemistry.

It was in Glasgow that Cecil Wilson's interests were first turned towards microchemistry, and as early as 1935 he designed and introduced an undergraduate course in this subject in Belfast. His first book, entitled "An Introduction to Microchemical Methods" was published in 1938. During the war he had to do mainly analytical—often microanalytical— work for the Ministry of Supply, and from this time his interest in analytical chemistry became dominating. In co-authorship with Professor R. Belcher he published a book on Inorganic Microanalysis in 1946, 2nd edition 1957, and a similar co-operation produced various editions of "New Methods of Analytical Chemistry". Although his interests in teaching and research in Analytical Chemistry were always predominant, he found time and energy to keep up with Inorganic and Physical Chemistry. At the request of his old Professor at Queen's, Dr Stewart, he collaborated on the 7th edition of "Recent Advances in Inorganic and Physical Chemistry", the 6th edition of which had been completely destroyed before publication, by fire during the London blitz. The book, published under the names of Stewart and Wilson, appeared in 1941. Later, with his colleague Barnett at Cass College, he produced the well-known textbook of Barnett and Wilson: Inorganic Chemistry.

As an Editor, Professor Wilson served the community of Analytical Chemists in many ways. He was elected to the editorial board of *Microchimica Acta* in 1949, and has served on it ever since; between 1955 and 1962 he also acted as regional editor for papers written in English. When *Talanta* was established in 1958 as a new journal for Analytical Chemistry, Cecil Wilson became its first Editor-in-Chief, acting as such up to 1964, and since then acting as consulting editor. In 1959, in collaboration with his brother, D. W. Wilson, he became editor of the series "Comprehensive Analytical Chemistry" and since its foundation in 1967 he has served on the editorial board of *Analytical Letters*.

The Society for Analytical Chemistry called upon Cecil Wilson's services on several occasions. He has served on the Council three times since 1951. He was a founding member of the Microchemical Group, and acted as Chairman for the same group in

1951–52. He is a Fellow of the Royal Institute of Chemistry and has acted for years as the Chairman of the Northern Ireland section. His growing international reputation led to Honorary Membership of the Austrian Microchemical Society in 1955, and he was elected to Membership of the Royal Irish Academy in 1966.

Although his duties as Professor and Head of Department leave little time for non-professional activities, he manages to find time to act as Document Examiner for the Ministry of Home Affairs of Northern Ireland, appearing frequently as expert witness in court proceedings. He has held this appointment since 1953. He also served for six years on the Northern Ireland regional Committee of the Independent Television Authority.

Cecil Wilson started to do research in microchemistry, microscopy, micro- and ultramicroanalysis, but his interests widened when he had the opportunity of building up his own Department and research school at Queen's. About 100 papers and more than 30 research students bear witness to these activities.

While congratulating him on his sixtieth birthday, we wish Cecil Wilson further successes in his wide range of activities.

GYULA SVEHLA

Talanta, 1972, Vol. 19, pp. iii to v. Pergamon Press. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Ultrapurity: Methods and Techniques. Ed. MORRIS ZIEF and ROBERT M. SPEIGHTS. Dekker, New York, 1972. Pp. 700. $37.50.

The subject matter of this book will be of interest to many analysts. Some of the articles are directly concerned with such associated problems as sources of contamination and choice of container materials for high-purity materials, but this should not be taken as an excuse for five additional chapters on commonly used analytical techniques. The exception is provided, however, by A. J. Barnard's stimulating survey "High-purity chemicals—a challenge to the practical analyst." The first eleven chapters are concerned with the preparation of a number of materials in high purity (alkali metal halides, sodium and potassium, solvents, P_2O_5, proteins, *p*-xylene, isopropylbenzene, cholesterol, and water) and with the use of some techniques for purification (GLC, fractional distillation, dry-column chromatography). There is much valuable information in this book, based on the personal experience of the authors, (the chapters on glass, silica and ceramics in particular).

Air Pollution. Part A: Analysis. JOE O. LEDBETTER. Dekker, New York, 1972. Pp. 424. $11.75.

The author makes a successful attempt to distinguish the real problems from the imaginary and to help the student appreciate the need for a clear understanding of what pollution is, and what kind of analytical data are likely to be useful to the controlling authorities. Topics covered include Sources of pollution, Atmospheric transport of pollutants, Statistical evaluation, Sampling, Properties of gaseous and particulate pollutants, and various aspects of the analytical methods used. This book can be recommended as interesting and worthwhile reading.

Electrochemistry: Calculations, Simulation and Instrumentation. (Computers in Chemistry and Instrumentation Series, Vol. 2) Ed. J. S. MATTSON, H. B. MARK, JR. and H. C. MACDONALD, JR. Dekker, New York, 1972. Pp. 466. $23.50.

The successful design and application of mathematical models has been a notable development in the study of electrochemical processes in recent years, being limited more by the complexity of the models than by their shortcomings. The contributors to this volume show how the use of computers can alleviate the problem of complexity and enable the chemist to design and test his mathematical models with ease. Thirteen chapters, contributed by sixteen authors, cover a wide variety of topics, some of rather specialized application, others, such as those on Numerical solution of integral equations, and Operational amplifier instruments for electrochemistry, may be commended as useful and readable introductions for the non-specialist. The offset-litho printing from the typescript—aimed at speeding up the publishing—suffers from a lack of variety in type faces which is particularly noticeable in chapters with a considerable mathematical content, and does not appear to effect any cost-saving.

Simplified Circuit Analysis: RICHARD B. SACKS and HARRY B. MARK, JR. Dekker, New York, 1972. Pp. 166. $6.50.

The two sections of this book, dealing with analogue and digital circuitry respectively, grew out of material presented in a course on basic electronics as applied to instrumentation and written for non-engineers. A special feature is the emphasis on circuit analysis by the Laplace Transform Method. There are many figures to illustrate the text, and examples are given of chemical applications—for example the solution of problems in kinetics by analogue computer.

Solvent Extraction Reviews Vol. 1: Ed. Y. MARCUS. Dekker, New York, 1972. $19.50.

The object of this new series of reviews is to provide authorative surveys and critical discussion of advances in the field of solvent extraction. Speedy publication is promised and future reviews will appear first in journal form and then in an annual hardback edition. The selection of items in this volume is diverse and covers discussion of extraction equilibrium and kinetics of organophosphorus acids, the extraction of protactinium and polonium, mixing equipment, mass transfer problems and the industrial extraction of phosphoric acid. The papers provide useful background reading for the analyst, although the bias is clearly towards the physico-chemical aspects of the technique. The emphasis on criticality however, is most welcome and future volumes may well have more contributions of direct analytical interest.

Etude analytique de dérivés fluorés: M. HANOCQ. Editions Arscia S.A., Brussels, and Librairie Maloine S.A. Paris, 1972. Pp. 241. 490 F.B.

This book contains a comprehensive account of the methods available for determination of fluoride (or fluorine) by spectrophotometry or potentiometry, with special reference to materials of biological or organic origin. In doing so it reports at some length original work from the author's laboratory, with statistical analysis of the results. In view of the author's undoubted interest in statistics, it seems curious to recommend optimum reaction conditions that apparently require very exact measurement of reagent volumes, and to state ratios of sensitivities to better than 1% relative. There is an English version of the summary of the book, and the publishers have done the author a disservice by not having the translation edited properly. Nevertheless the book as a whole is a useful summary of the present state of determination of fluorine in fluorinated compounds.

Luminescence Spectrometry in Analytical Chemistry. J. D. WINEFORDNER, S. G. SCHULMAN and T. C. O'HAVER. Wiley-Interscience, New York, 1972. Pp. xiii + 354. $19.95.

The senior author of this work is well known for his contributions to interpretations of errors in luminescence spectrometry and for his practical application of absorption and fluorescence, and this book amply reflects his interests, the first two thirds being devoted mainly to theory, whether of the basic phenomena or of the instrumentation, and the remainder to a review of the analytical applications. In view of the increasing interest in the technique it is a pity that the literature coverage appears to stop at 1969 except for a few references to work undertaken by the author(s) or described at meetings. The book will prove very useful to analysts working in this field.

Analytical Applications of EDTA and Related Compounds. R. PŘIBIL. Pergamon, Oxford, 1972. Pp. xxi + 368. £12·50.

The title of this book is slightly misleading, as the book does not deal at all with the direct application of EDTA and its analogues as titrants, but is concerned with their use as masking agents in gravimetric, titrimetric and colorimetric analysis, and with the use of metallochromic indicators as reagents in colorimetry. In addition there is mention of the solvent extraction of some metal complexes of these compounds. As might be expected from the author, there is a wealth of detail on practical application. The literature coverage stops at around 1967–8, largely because the author considers that practically all the important work had already been done by then. The book will prove a valuable reference work for all analysts concerned with inorganic analysis.

Marine Chemistry, Vol. 1, Analytical Methods. DEAN F. MARTIN, 2nd Ed. Dekker, New York, 1972. Pp. viii + 389. $9.50.

The fact that a second edition (expanded and revised) has been found necessary only four years after the appearance of the first doubtless reflects the interest taken in the chemistry of the ocean. The literature coverage has been brought up to date (up to late 1971).

Analytical Atomic Absorption Spectrometry: W. J. PRICE, Heyden, London, 1972. Pp. xii + 239 £5·80, $15.25.

Those familiar with the very extensive range of monographs on atomic-absorption spectrometry might well be excused for expressing dismay at the introduction of yet another work on this subject. It is therefore extremely gratifying to be able to report that this volume is undoubtedly one of the finest and most concise and readable expositions of atomic-absorption currently available. Selection of material and the level of treatment used clearly represent the results of a good deal of careful and painstaking thought and effort on the part of the author, who has produced a book which should serve for several years to come as an invaluable reference work for the analyst, regardless of his previous experience of the technique. The excellent résumé of sample dissolution methods for a wide range of sample types renders the book an asset not only in all branches of analytical flame spectrometry, but also in many other branches of analytical chemistry.

Annual Reports on Analytical Atomic Spectroscopy, Vol. 1: D. P. HUBBARD (Ed.), The Society for Analytical Chemistry, London, 1971. Pp. 204. £5·00, $13.00.

Much credit must go to the editor and editorial board of the first volume of this annual series for the promptness of publication which has resulted in a useful outline of the developments in all major branches of analytical atomic-spectroscopy during 1971, with few of the errors and omissions which are perhaps inevitable in a work of this kind. Particularly useful are the references to papers presented at conferences and to papers published in some of the less readily available journals. These, together with the frequent use of tabular presentation of data selected from a wide range of sources indicate that this inexpensive book should prove to be a valuable source of reference to spectroscopists engaged in both routine analysis and in academic and more applied research.

Bibliography of Paper and Thin Layer Chromatography 1966–1969, Journal of Chromatography, Supplementary Volume No. 2: edited by K. MACEK, I. M. HAIS, J. KOPECKÝ, J. GASPARIČ, V. RÁBEK and J. CHURÁČEK, Elsevier, Amsterdam, 1972. Pp. XVI + 991. Dfl. 200.00, $*ca.* 62.50.

The editors and those who collaborated in the production of this bibliography on paper and thin-layer chromatography have performed a daunting and arduous task. They have sifted the contents of countless papers, many of them in journals not readily available. This work lists papers deemed particularly significant. The titles, unless originally in English, German or French, have been translated and, in the case of the less readily available journals, references to *Chemical Abstracts* are commonly included. Over the past decade the *Journal of Chromatography* has published bibliographies on the fields covered by the present work. Now the collective labours for the years 1966–69 have been brought together in augmented, critically selected, rearranged and well-ordered form. There are 849 references to papers on general methods followed by 7846 references to compounds classified in about 500 groups. Such a book needs, and has, lengthy, comprehensive and reliable compound and author indices. There are also helpful cross-references at the end of each section to papers listed elsewhere in the book. Bibliographies are not for readers, but for the guidance of those lost or uncertain where to turn. This chromatographic gazetteer will save many travellers in the field much unnecessary toil and with, or without, a preceding volume covering the years 1961–65 will, it is to be hoped, justify the cost of placing it on the shelves of every library frequented by research workers using such chromatographic methods.

Neutron Activation Analysis: D. DE SOETE, R. GIJBELS and J. HOSTE. Wiley-Interscience, London, 1972. Pp. xx + 836. £14.

This comprehensive treatise upon the most important technique of trace analysis constitutes Volume 34 of the series of monographs edited by P. J. Elving and I. M. Kolthoff under the general title of Chemical Analysis. There is an introductory section describing the scope and application of the technique and this is followed by chapters dealing with the theoretical aspects of the interaction of neutrons with nuclei. Succeeding chapters outline the experimental methods and describe neutron sources, the growth and decay of induced radioactivity and the detection of the resulting radioelements. In addition, the preparation of samples and standards is described, together with procedures for chemical segregation of activities. The book closes with a survey of systematic errors and the statistical analysis of experimental results. There is an extensive bibliography classified in tabular form under author's name and element determined, and appendices containing lists of neutron cross-sections.

Photoelectron Spectroscopy: A. D. BAKER and D. BETTERIDGE. Pergamon, Oxford, 1972. Pp. x + 180. £3·50.

This is the first book dealing explicitly with the analytical applications of one of the most recent additions to spectroscopy. The theory of the photoelectric effect is outlined and there is a detailed discussion of instrumentation. The appearance and interpretation of photoelectron spectra are described with reference to the detailed fine structure. Although the book is mainly concerned with electron emission resulting from the absorption of X-ray and ultraviolet photons there is a section dealing with other techniques based upon the energy analysis of emitted electrons. There are appendices giving lists of ionization potentials and orbital energies.

EDITORIAL

SI UNITS

In 1968 the Royal Society Committee of Editors decided that as a matter of policy their journals would use SI units in future. The International Union of Pure and Applied Chemistry also gave its support to exclusive use of SI units. Because *Talanta* has always followed the recommendations of IUPAC, an editorial in the 1968 July issue informed readers that SI units would be used in this journal. Three years later, we have received a grand total of two papers actually written with use of SI units only, and it is clear that whatever the future may hold in the shape of papers written by scientists trained from childhood in the use of SI, the current generation of practising analysts will have no truck with the system. We shall therefore revert to allowing authors to use the units that are familiar to them and which are in everyday use on instrument dials *etc*, with some exceptions in the case of units that are unnecessary duplication of existing and more immediately understood units. Examples are "mil" (instead of 0.001 in.) and "torr" (instead of mmHg). We shall continue to use milliard (abbreviation M) for 10^9 to avoid the confusion between American and European billions, and mole for an Avogadro's number of units of the species named (the IUPAC abbreviation to "mol" seems singularly pointless). By a happy coincidence, the two papers that *were* written in terms of SI units also were the two best-written papers published in *Talanta* in 1971, and it is with pleasure that we announce the joint award of the Louis Gordon Memorial Award to Mrs. Elsie M. Donaldson, of Ottawa, Canada, for her paper on "Determination of aluminium in molybdenum and tungsten metals, iron, steel and ferrous and non-ferrous alloys with Pyrocatechol Violet" (*Talanta*, 1971, **18**, 905) and to Dr. G. B. Briscoe and Dr. S. Humphries, of Birmingham, England, for their paper on "Substoichiometric determination of traces of palladium by radioactive isotope-dilution analysis" (*Talanta*, 1971, **18**, 39).

Volume 19, 1972

July–December, Nos. 7–12

CONTENTS

NUMBER 7

Short Communications

Annotation

NUMBER 8

Short Communications

NUMBER 9

Note

Letter to the Editor

NUMBER 10

Short Communications

Analytical Data

NUMBER 11

Short Communications

Analytical Data

Annotations

NUMBER 12

Short Communications

Analytical Data

Annotations

SUMMARIES FOR CARD INDEXES

Determination of trace elements in metals and alloys by atomic-absorption spectroscopy using an induction-heated graphite well furnace as atom source: J. B. HEADRIDGE and DAVID RISSON SMITH, *Talanta*, 1972, **19**, 833 (Chemistry Department, Sheffield University, Sheffield, S3 7HF, U.K.)

Summary—An induction-heated graphite furnace, coupled to a Unicam SP 90 atomic-absorption spectrometer, is described for the direct determination of trace elements in metals and alloys. The furnace is capable of operation at temperatures up to 2400°, and has been used to obtain calibration graphs for the determination of ppm quantities of bismuth in lead-base alloys, cast irons and stainless steels, and for the determination of cadmium at the ppm level in zinc-base alloys. Milligram samples of the alloys were atomized directly. Calibration graphs for the determination of the elements in solutions were obtained for comparison. The accuracy and precision of the determination are presented and discussed.

Separation of the non-volatile noble metals by reversed-phase extraction chromatography: CHRISTEL POHLANDT and T. W. STEELE, *Talanta*, 1972, **19**, 839. (National Institute for Metallurgy, Private Bag 6, Johannesburg, South Africa.)

Summary—The procedure involves the use of tri-n-butyl phosphate (TBP) adsorbed by Porasil C and stepwise elution with sulphuric acid and hydrochloric acid. The distribution coefficients for the two systems (TBP and hydrochloric acid and TBP and sulphuric acid) and the elution characteristics were studied. A description is given of a procedure applicable to the analysis of prills obtained from the fire assay of platinum-bearing ores.

Determination of trace amounts of uranium in silicate minerals by the fission track technique: HIDEKI, MATSUDA, YUTAKA TSUTSUI, SHIGENORI NAKANO and SHUNJI UMEMOTO, *Talanta*, 1972, **19**, 851. (Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka, Japan.)

Summary—The fission track technique has been applied to the determination of uranium on Dowex 1 × 8 after chemical separation from silicates. Standard rock and several stone meteorite samples were treated by this method and satisfactory results were obtained. The procedure is applicable to natural waters.

ОПРЕДЕЛЕНИЕ СЛЕДОВ ЭЛЕМЕНТОВ В МЕТАЛЛАХ И СПЛАВАХ МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ ГРАФИТНОЙ ПЕЧИ С ИНДУКЦИОННЫМ НАГРЕВАНИЕМ В КАЧЕСТВЕ ИСТОЧНИКА АТОМОВ:

J. B. HEADRIDGE and DAVID RISSON SMITH, *Talanta*, 1972, **19**, 833.

Резюме—Описана графитная печь с индукционным нагреванием, комбинированная с атомно-абсорбционным спектрофотометром Юникам СП 90, для непосредственного определения следов элементов в металлах и сплавах. Печь позволяет нагревать пробы вплоть 2400° и использована для получения калибровочных кривых для определения микрограммовых количеств висмута в сплавах на основе свинца, в чугуне и нержавеющих сталях и для определения частей на миллион кадмия в сплавах на основе цинка. Метод позволяет распылять непосредственно миллиграмовые количества сплавов. Результаты сравнены с калибровочными кривыми полученными для растворах элементов. Приведены и обсуждены точность и воспроизводимость результатов.

РАЗДЕЛЕНИЕ НЕЛЕТУЧИХ БЛАГОРОДНЫХ МЕТАЛЛОВ МЕТОДОМ ЭКСТРАКЦИОННОЙ ХРОМАТОГРАФИИ С ОБРАТНОЙ ФАЗОЙ:

CHRISTEL POHLANDT and T. W. STEELE, *Talanta*, 1972, **19**, 839.

Резюме—Метод использует три-н-бутилфосфат (ТБФ) адсорбированный на Порасиле С и этапное элюирование серной и соляной кислотами. Изучены коэффициенты распределения для этих двух систем (ТБФ—соляная кислота и ТБФ—серная кислота) и характеристики элюирования. Описан метод применимый в анализе королков полученных при испытании сухим путём платинусодержащих руд.

ОПРЕДЕЛЕНИЕ СЛЕДОВЫХ КОЛИЧЕСТВ УРАНА В СИЛИКАТНЫХ МИНЕРАЛАХ МЕТОДОМ СЛЕДА ФИССИИ:

HIDEKI MATSUDA, YUTAKA TSUTSUI, SHIGENORI NAKANO and SHUNJI UMEMOTO, *Talanta*, 1972, **19**, 851.

Резюме—Метод следа фиссии применен в определении урана на смоле Дауекс 1 × 8 после химического отделения от силикатов. Эталонные горные породы и некоторые образци каменных метеоритов анализированы с помощью этого метода и получены удовлетворительные результаты. Методом можно пользоваться для анализа природных вод.

Rapid mass-spectrometric determination of boron isotopic distribution in boron carbide: James E. Rein and Robert M. Abernathey, *Talanta*, 1972, **19**, 857. (University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, U.S.A.)

Summary—Boron isotopic ratios are measured in boron carbide by thermionic ionization mass spectrometry with no prior chemical separation. A powder blend of boron carbide and sodium hydroxide is prepared, a small portion is transferred to a tantalum filament, the filament is heated to produce sodium borate, and the filament is transferred to the mass spectrometer where the $^{11}B/^{10}B$ ratio is measured, using the $Na_2BO_2^+$ ion. Variables investigated for their effect on preferential volatilization of ^{10}B include the sodium hydroxide–boron carbide ratio and the temperature and duration of filament heating. A series of boron carbide pellets containing natural boron, of the type proposed for the control rods of the Fast Flux Test Facility reactor, were analysed with an apparently unbiased result of 4·0560 for the $^{11}B/^{10}B$ ratio (standard deviation 0·0087). The pellets contained over 3% metal impurities typically found in this material. Time of analysis is 45 min per sample, with one analyst.

Determination of niobium in rocks, ores and alloys by atomic-absorption spectrophotometry: John Husler, *Talanta*, 1972, **19**, 863. (Department of Geology, University of New Mexico, Albuquerque, New Mexico 87106, U.S.A.)

Summary—Niobium, in concentrations as low as 0·02% Nb_2O_5, is determined in a variety of materials without separation or enrichment. Chemical and ionization interferences are controlled, and sensitivity is increased, by maintaining the iron, aluminium, hydrofluoric acid and potassium content within certain broad concentration limits. There is close agreement with the results of analyses by emission spectrographic, electron microprobe and X-ray fluorescence methods.

Constitution and stability of acidic periodate solutions: D. J. B. Galliford, R. H. Nuttall and J. M. Ottaway, *Talanta*, 1972, **19**, 871. (Chemistry Department, University of Strathclyde, Cathedral Street, Glasgow C.1, Scotland.)

Summary—Acidic periodate solutions are shown to contain two species, tetrahedral IO_4^- and octahedral H_5IO_6. Equilibrium between the two is attained rapidly and the solutions are stable for long periods of time if stored in amber glass bottles.

БЫСТРОЕ ОПРЕДЕЛЕНИЕ РАСПРЕДЕЛЕНИЕ ИЗОТОПОВ БОРА В КАРБИДЕ БОРА МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ:

JAMES E. REIN and ROBERT M. ABERNATHY, *Talanta*, 1972, **19**, 857.

Резюме—Отношения изотопов бора в карбиде бора измерены методом масс-спектрометрии с термоионной ионизацией без предварительного химического разделения. Приготовляют порошковидную смесь карбида бора и гидроокиси натрия, небольшую часть переносят на танталовую нить, нить нагревают для получения бората натрия и нить переносят в масс-спектрометр. Измеряют отношение $^{11}B/^{10}B$ с использованием иона $NaBO_2^+$. Изучены факторы влияющие на селективное улетучивание ^{10}B, так как отношение гидроокиси натрия и карбида бора, температура и продолжительность нагревания нити. Анализ ряда гранул карбида бора содержаших природный бор, типа предложенного для контрольных прутков реактора Fast Flux Test Facility дал очевидно беспристрастный результат 4,0560 для отношения $^{11}B/^{10}B$ (стандартная ошибка 0,0087). Гранулы содержали больше чем 3% примесей металлов, типических дла этого материала. Продолжительность анализа 45 на образец, с одним аналитиком.

ОПРЕДЕЛЕНИЕ НИОБИЯ В ГОРНЫХ ПОРОДАХ, РУДАХ И СПЛАВАХ МЕТОДОМ АТОМНО-АБСОРБДИОННОЙ СПЕКТРОФОТОМЕТРИИ:

JOHN HUSLER, *Talanta*, 1972, **19**, 863.

Резюме—Ниобий определяют в концентрациях вплоть до 0,02% Nb_2O_5 в разных материалах без предварительного выделения или обогащения. Химические и ионизационные действия предотвращаются а чувствительность повышается поддерживанием содержания железа, алюминия, фтористо-водородной кислоты и калия в известных широких диапазонах концентраций. Полученные результаты хорошо соглашаются с результатами полученными методами эмиссионной спектрографии, электронной микропробы и рентгеновской флуоресценции.

СТРОЕНИЕ И УСТОЙЧИВОСТЬ КИСЛЫХ РАСТВОРОВ ПЕРИОДАТА:

D. J. B. GALLIFORD, R. H. NUTTALL and J. M. OTTAWAY, *Talanta*, 1972, **19**, 871.

Резюме—Показано что кислые растворы периодата содержают две формы—тетраэдрическую IO_4^- и октаэдрическую H_5IO_6. Равновесие между этим двумя формами быстро устанавливается и растворы являются устойчивыми через долгие периоды времени если сохраняются в янтарных стеклянных склянках.

Complexation of polyvinyl alcohol with iodine. Analytical precision and mechanism: J. G. Pritchard and D. A. Akintola, *Talanta*, 1972, **19**, 877. (North East London Polytechnic, London, E. 15, U.K.)

Summary—Polyvinyl alcohol (PVA), boric acid and tri-iodide form a characteristic blue complex. For a number of PVA samples, prescribed conditions were used to examine the precision of the formation and spectrophotometry of the complex. The precision of calibration curves was 1–2% over the range 0–4 mg of PVA per 50 ml of final solution, over which Beer's law holds. Greater deviations can be caused by faulty preparation and aging of individual PVA solutions. The absorbance is independent of the content of residual acetate groups in the PVA for the range 0–15%. The limit of detection is about 0.01 mg of PVA in 25 ml of sample. A pink colour in the system is due to association of iodine with acetate groups in the PVA. A blue or green colour is due to helical envelopment of iodine molecules by PVA chains stiffened by scattered cyclic groups. The mechanisms of these effects are discussed.

Liquid-liquid interfaces as potentiometric ion-sensors—I. The n-butanol–water interface as indicating sensor for the potentiometric titration of some acids and bases: Candin Liteanu and Maria Mioşcu, *Talanta*, 1972, **19**, 889. (Department of Analytical Chemistry, University of Cluj, Romania.)

Summary—The property that liquid—liquid interfaces modify their electrical charge as a function of the composition of the two phases in contact has been used to detect the end-points in a series of acid–base titration in the aqueous phase. Although the titration curves are not classical in shape, the equivalence points can be located if the solutions are not too dilute. Good results for concentrations down to $10^{-3}N$ have been obtained. The electrode has a fast response. The influence of surface-active substances on the titration has also been investigated.

Studies on nucleation from solution of some analytically important metal chelates—II. Nickel dimethylglyoximate. J. D. Hanna and O. E. Hileman, Jr.®, *Talanta*, 1972, **19**, 894 (Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.)

Summary—A new direct-mixing and rapid particle-counting system useful for studies on crystal nucleation from solution is described. The methods used to calibrate and evaluate the system are reported together with the results obtained during studies on nucleation from solution of nickel dimethylglyoximate. The Volmer-Weber, Becker-Döring model of the nucleation process is used to correlate the results.

Losses of iridium during heating in various atmospheres: A. Chow *Talanta*, 1972, **19**, 899. (Department of Chemistry, University of Manitoba, Winnipeg 19, Manitoba, Canada.)

Summary—The volatility of iridium metal in different atmospheres was studied, using various weights, times and temperatures. Significant volatility was observed in oxygen and oxygen plus acid at temperatures above 400° and in chlorine above 220°

ОБРАЗОВАНИЕ КОМПЛЕКСОВ ПОЛИВИНИЛОВОГО СПИРТА С ИОДОМ. ТОЧНОСТЬ ОПРЕДЕЛЕНИЯ И МЕХАНИЗМ:

J. G. Pritchard and D. A. Akintola, *Talanta*, 1972, **19**, 877.

Резюме—Поливиниловый спирт (ПВС), борная кислота и трииодид образуют характеристический голубой комплекс. Использованы определенные условия для испытания воспроизводимости образования комплекса и его спектрофотометрических характеристик на ряде образцов ПВС. Воспроизводимость калибровочных кривых была 1–2% в пределах 0–4 мг ПВС в 50 мл конечного раствора, в которых пределах почитается закон Бера. Большие ошибки могут быть вызваны неисправным приготовлением и старением растворов ПВС. Светопоглощение независимо от содержания остаточных ацетатных групп в ПВС в пределах 0–15%. Чувствительность равна 0,01 мг ПВС в 25 мл раствора пробы. Розовый цвет появляется в системе вследствие ассоциации иода с ацетатными группами в ПВС. Голубой или зелёный цвет появляется в результате спирального обёртывания молекул иода цепями ПВС, усиленными рассеянными циклическими группами. Рассмотрены механизмы этих эффектов.

ПОВЕРХНОСТЬ РАЗДЕЛА МЕЖДУ ЖИДКОСТЯМИ В КАЧЕСТВЕ ПОТЕНЦИОМЕТРИЧЕСКОГО ДАТЧИКА ДЛЯ ИОНОВ—I. ПОВЕРХНОСТЬ РАЗДЕЛА МЕЖДУ Н-БУТАНОЛОМ И ВОДОЙ В КАЧЕСТВЕ ИНДИКАТОРНОГО ДАТЧИКА ДЛЯ ПОТЕНЦИОМЕТРИЧЕСКОГО ТИТРОВАНИЯ НЕКОТОРЫХ КИСЛОТ И ОСНОВАНИЙ:

Candin Liteanu and Maria Mioscu, *Talanta*, 1972, **19**, 889.

Резюме—Свойство поверхности раздела между жидкостями изменять их электрический заряд в зависимости от состава этих двух фаз в контакте использовано для обнаружения конца титрования в ряде кислотно-щелочных титраций в водной фазе. Титрационные кривые не показывают классическую форму, однако возможно обнаружить конец титрования если растворы не слишком разбавлены. Получены хорошие результаты вплоть до концентрации 10^{-3} *N*. Электрод обладает быстрым ответом. Также изучено влияние поверхностно-активных веществ на титрование.

ИЗУЧЕНИЕ НУКЛЕАЦИИ ИЗ РАСТВОРА НЕКОТОРЫХ ПРИМЕНИМЫХ В АНАЛИЗЕ ХЕЛАТОВ МЕТАЛЛОВ—II. ДИМЕТИЛГЛИОКСИМАТ НИКЕЛЯ.

J. D. Hanna and O. E. Hileman, *Talanta*, 1972, **19**, 894.

Резюме—Новая система непосредственного смешивания и быстрого счёта частиц оказалась полезной в изучении нуклеации кристаллов из растворов. Рассмотрены методы калибровки и оценки системы, вместе с результатами полученными в изучении нуклеации из раствора диметилглиоксимата никеля. Модель Вольмера-Вебера, Бекера-Доринга процесса нуклеации использована для сравнения результатов.

ПОТЕРИ ИРИДИРЯ ПРИ НАГРЕВАНИИ В РАЗНЫХ АТМОСФЕРАХ:

A. Chow, *Talanta*, 1972, **19**, 899.

Резюме—Изучена летучесть металлического иридия в разных атмосферах, с использованием различных весов, продолжительностей и температур. Обнаружена значительная летучесть в кислороде и в кислороде в присутствии кислоты при температурах выще 400°, и в хлоре выше 220°.

NOTES FOR AUTHORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable. Original papers, preliminary and short communications, annotations, reviews, and letters will be published.

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in **any language**, that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical.** The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists. Annotations should be critical commentaries on some aspects of analytical chemistry and may deal with topics such as sources of error, or the scope and limitations of methods and techniques.

Original papers, short communications annotations and reviews will be refereed (see *Talanta*, 1962, **9**, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

Preliminary communications will be refereed urgently and will be accorded priority in publication. Letters to the Editor will not be refereed, but will be published at the discretion of the Editor-in-Chief. If accepted, they will also be given priority.

Fifty free reprints will be provided (regardless of the number of authors) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

By following the Script Requirements carefully, authors will ensure more rapid publication of their papers.

General

Contributions should be submitted to the Editor-in-Chief or to a Regional Editor where appropriate (see editorial page for addresses). They may be written in English, French or German. All contributions in the French language should be submitted to Dr. M. Pesez, and those in the German language to Professor E. Blasius.

Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfil these conditions they will be treated as short communications.

Scripts should be submitted in duplicate; they should be typewritten and the lines double-spaced. Where possible, papers should follow the pattern: *Introduction*, *Experimental*, *Results*, *Discussions*, *Conclusions* (or such of these headings as apply).

Because all material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors writing in a foreign language are advised that in submitting papers they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for retyping, resulting in a serious delay in publication.

Summaries

The essential contents of each paper should be briefly recapitulated in a summary **placed at the beginning of a paper, or at the end of a preliminary or short communication.** This should be in the language of the paper, but for French or German papers an English version should also be provided wherever possible.

Illustrations

Illustrations should be separate from the typescript of the paper. Original line drawings should be supplied (about twice the final size required) together with one set of copies. **If the illustrations require redrawing, publication of the paper will be delayed.** The following standard symbols should be used on line drawings:

△ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⌽ ⊗

Photographs should be restricted to the very minimum required.

Legends for illustrations should be typed on a separate sheet.

Straight-line calibration graphs are not generally permitted; the necessary information can usually be included in the text (*e.g.* in the form of an equation).

Tables should be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarize results by an accepted method of expression (*e.g.* standard deviation). The same information should not be produced in both tables and figures.

The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

References

References should be indicated in the text by consecutive superior numbers placed outside any punctuation marks; the full references should be given in a list at the end of the paper in the following form:

1. J. B. Austin and R. H. H. Pierce, *J. Am. Chem. Soc.*, 1955, **57**, 661.
2. S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*, 2nd Ed., Vol. 3, p. 214. Pergamon Press, Oxford, 1956.
3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strength of Metals.* A.E.R.E., M/R 6329, 1962.
5. W. Jones, *Brit. Pat.* 654321, 1959.

Journal-name abbreviations should be those used in *Chemical Abstracts* (see *Chem. Abstr.*, 1961, *et seq.*).

Footnotes to pages and to tables, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, beginning anew on each page.

Proofs

Proofs are not set in galley form and will be sent out to authors in page form for correction. **It is emphasized that at this stage alterations to the text or failure to return the corrected proofs promptly may result in serious delay in publication, and authors will be charged for changes other than printers' errors.**

Authors are particularly requested to check the correctness of their references, which should also, at some stage, be checked against the original papers.

Miscellaneous

Because of the international character of the journal, authors should follow the recommendations of the *International Union of Pure and Applied Chemistry* as regards nomenclature and symbols. In the editing of papers for publication, English spelling will be used for all matter in the English language. Authors who wish to retain American spelling, or to adhere to other generally accepted usages, should indicate this clearly at the time of submission of the manuscript. Attention is particularly drawn to the importance of correctness of grammar and clarity of expression.

Where several authors are involved in a paper, an indication of the author to whom requests for reprints should be addressed may be given by placing the symbol ® after the name of that author.

Des exemplaires en français des Notes aux Auteurs peuvent être obtenus auprès du Rédacteur en Chef

Deutsche Abdrucke der Anmerkungen für Mitarbeiter sind beim Hauptschriftleiter zu erhalten

Оттиски правил для авторов на русском языке можно получить у главного редактора

AUTHOR INDEX

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST

Reprints of the following reviews published in Talanta are available from Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, or Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

1 **Precipitation of Metal Chelates from Homogeneous Solution** by F. H. Firsching

2 **Recent Developments in the Ring Oven Technique** by H. Weisz

3 **Adsorption Indicators in Precipitation Titrations** by R. C. Mehrotra and K. N. Tandon

4 **Radiometric Titrations** by T. Braun and J. Tölgyessy

5 **Recent Uses of Liquid Ion Exchangers in Inorganic Analysis** by H. Green

6 **Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry** by B. D. Flockhart and R. C. Pink

7 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum** by F. E. Beamish

8 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold** by F. E. Beamish

9 **Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals** by R. Přibil

10 **Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique** by F. Girardi

11 **Separation of Transplutonium Elements** by J. Starý

12 **Differential Spectrophotometry** by G. Svehla

13 **A Critical Review of Gravimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

14 **A Critical Review of Titrimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

15 **Present State of Complexometry—II: Determination of Bivalent Metals** by R. Přibil

Reprints of Talanta Reviews

As the volume of scientific literature grows, reviews provide one of the best means of keeping abreast with recent developments. Talanta has commissioned a series of comprehensive and critical reviews of topics of current interest to analytical chemists; many of these reviews will also be of value to chemists in general and to other scientists. Talanta Reviews are intended primarily to introduce the non-specialist to a subject about which he previously knew little, but they may also help the specialist fill gaps in his knowledge of his own field or illuminate the subject from a new angle.

16 **Derivatography: A Complex Method in Thermal Analysis**
by F. Paulik, J. Paulik and L. Erdey

17 **Potassium Dichromate as an Oxidimetric Reagent**
by G. Gopala Rao

18 **Newer Acylation Methods for the Determination of Organic Hydroxyl and Amino Compounds**
by N. K. Mathur

19 **A Critical Review of Neutron Activation and Tracer Methods for the Determination of the Noble Metals**
by F. E. Beamish, K. S. Chung and A. Chow

20 **Process Gas Chromatography**
by C. S. F. Pine

21 **Present State of Complexometry—III and IV: Determination of Univalent Metals and Determination of Rare Earths**
by R. Přibil

22 **A Critical Review of Methods of Isolating and Separating the Noble Metals—II: Ion Exchange and Solvent Extraction**
by F. E. Beamish

23 **A Critical Review of Methods of Isolating and Separating the Noble Metals—III: Chromatography, Precipitation and Fire Assay**
by F. E. Beamish

24 **Complexation Reactions of Dithiocarbamates**
by A. Hulanicki

25 **Polarographic Behaviour of Metal Chelates of *o,o'*-Dihydroxyazo Dyes**
by G. W. Latimer, Jr.

26 **Characteristic Metal–Halogen Vibrational Frequencies of Complexes with Bivalent Metal Halides**
by R. H. Nuttall

27 **Amplification Reactions**
by R. Belcher

28 **Ternary Complexes in Analytical Chemistry**
by A. K. Babko

29 **Determination of Antioxidants in Polymeric Materials**
by D. A. Wheeler

30 **A Critical Review of Atomic Absorption, Spectrochemical, and X-ray Fluorescence Methods for the Determination of the Noble Metals—II**
by F. E. Beamish, C. L. Lewis and J. C. Van Loon

31 **Applications of Digital Computers in Analytical Chemistry—I**
by C. W. Childs, P. S. Hallman and D. D. Perrin

32 **Applications of Digital Computers in Analytical Chemistry—II**
by C. W. Childs, P. S. Hallman and D. D. Perrin

33 **Fluorescence Analysis in Air Pollution Research**
by E. Sawicki

34 **Radioactive Kryptonates and Their Uses in Chemical Analysis**
by J. Tölgyessy and Š. Varga

35 **Quantitative Analysis in Pharmacy and Pharmaceutical Chemistry by Nuclear Magnetic Resonance Spectroscopy**
by D. M. Rackham

36 **Recent Developments in Substoichiometric Analysis**
by J. Starý and J. Růžička

continued overleaf

37 **Analytical and Experimental Aspects of Molecular-Sieve Chromatography**
by D. M. W. Anderson, I. C. M. Dea and A. Hendrie

38 **Use of Basic Dyes in the Determination of Anions, Particularly as a Means of Determining Antimony, Thallium, and Gallium**
by A. G. Fogg, C. Burgess and D. Thorburn Burns

39 **Organic Analysis by Luminescence Methods**
by J. Bartos and M. Pesez

40 **Synthetic Inorganic Ion-Exchangers—I. Hydrous Oxides and Acetic Salts of Multivalent Metals**
by V. Veselý and V. Pekárek

41 **Analytical Mass Spectrometry**
by J. R. Majer

42 **Reaction Rate Methods in Analysis**
by H. B. Mark, Jr.

43 **Synthetic Inorganic Ion Exchangers—II. Salts of Heteropolyacids, Insoluble Ferrocyanides, Synthetic Aluminosilicates and Miscellaneous Exchangers**
by V. Pekárek and V. Veselý

44 **Extreme Trace Analysis of the Elements—I. Methods and Problems of Sample Treatment, Separation and Enrichment**
by Günther Tölg

45 **Determination of Water**
by Clifford Harris

£0·50 or $1.50 each

Pergamon Press

Headington Hill Hall
Oxford, England

Maxwell House,
Fairview Park, Elmsford,
New York 10523, U.S.A.

ORDER FORM Date............

(Customers in America and Canada should return this form to the New York address)

Please send ......copy/copies of the following Talanta Reviews (please list numbers)

....

for which I enclose £................ $................

Name..

Address...

....

....

SUMMARIES FOR CARD INDEXES

Analytical mass spectrometry: J. R. MAJER, *Talanta*, 1972, **19**, 589. (Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.)

Summary—A review is made of the basic theory, instrumentation and application of mass spectrometry, with special reference to the development of the equipment and its impact on the scope of application.

Development and publication of work with selective ion-sensitive electrodes: G. J. MOODY and J. D. R. THOMAS, *Talanta*, 1972, **19**, 623. (University of Wales Institute of Science and Technology, Cardiff, Wales.)

Summary—Features concerning development, response, selectivity and applications of selective ion-sensitive electrodes are reviewed. Recommendations are made concerning investigations involving the development and applications of electrodes and attention given to the manner of presenting data for publication.

Iodometric microdetermination of sulphur in organic compounds by an amplification method: Y. A. GAWARGIOUS and A. B. FARAG, *Talanta*, 1972, **19**, 641. (Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, U.A.R.)

Summary—A new method is described for the iodometric microdetermination of sulphur in organic compounds, using a 12-fold amplification reaction after oxygen-flask combustion. The method is based on reaction of the resulting sulphuric acid with an excess of saturated barium bromate solution. The unreacted barium bromate is precipitated by addition of acetone, filtered off, redissolved in hot water and after addition of an excess of iodide and acid, the iodine liberated is titrated with thiosulphate. The method is simple, rapid, highly accurate, and of wide application in the microanalysis of organosulphur compounds containing other common acid-forming elements.

Improved synthesis and stability of 8-selenoquinoline and its sodium salt as organic reagents: EIICHI SEKIDO and ISAMU FUJIWARA, *Talanta*, 1972, **19**, 647. (Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan).

Summary—The synthesis of 8-selenoquinoline and its sodium salt has been improved by optimization of each process. The stability of the reagents in air and nitrogen has been examined and correlated with the drying method. Both 8-selenoquinoline and its sodium salt can exist as the monohydrate. It was found that the sodium salt of 8-selenoquinoline monohydrate is best as the weighing form of the reagent and that it can be kept stable under nitrogen in a vessel containing silica gel.

МАСС-СПЕКТРОМЕТРИЯ В АНАЛИЗЕ:

J. R. Majer, *Talanta*, 1972, **19**, 589.

Резюме—Приведен обзор основной теории, прибора и применения масс-спектрометрии, с особым учетом разработки аппаратуры и его эффекта на область применения метода.

РАЗРАБОТКА И ОПУБЛИКОВАНИЕ РАБОТ ПОЛЬЗУЮЩИСЯ ИОНОИЗБИРАТЕЛЬНЫМИ ЭЛЕКТРОДАМИ:

G. J. Moody and J. D. R. Thomas, *Talanta*, 1972, **19**, 623.

Резюме—Приведен обзор разработки, ответа, избирательности и применения ионоизбирательных электродов. Предложены исследования в области разработки и применения электродов и указаны пути приведения данных в статях.

МИКРОМЕТОД ИОДОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ СЕРЫ В ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ С ИСПОЛЬЗОВАНИЕМ АМПЛИФИКАЦИИ:

Y. A. Gawargious and A. B. Farag, *Talanta*, 1972, **19**, 641.

Резюме—Описан новый микрометод для иодометрического определения серы в органических соединениях, пользующийся 12-кратной амплификационной реакцией после сожжения в кольбе, наполненной кислородом. Метод основан на реакции образующейся серной кислоты с избытком насыщенного раствора бромата бария. Нереагированный бромат бария осаждают добавлением ацетона, фильтрируют, осадок растворяют в кипящей воде и—после добавления избытка иодида и кислоты—выделенный иод титрируют раствором тиосульфата. Метод оказался несложным, быстрым и весьма точным; он широко применим в микроанализе органических соединений серы, содержащих другие обыкновенные образующие кислоты элементы.

УЛУЧШЕННЫЙ СИНТЕЗ И СТАБИЛЬНОСТЬ 8-СЕЛЕНОХИНОЛИНА И ЕГО НАТРИЕВОЙ СОЛИ В КАЧЕСТВЕ ОРГАНИЧЕСКИХ РЕАГЕНТОВ:

Eiichi Sekido and Isamu Fujiwara, *Talanta*, 1972, **19**, 647.

Резюме—Синтез 8-селенохинолина и его натриевой соли улучшен путем оптимизации каждого процесса. Испытана устоичивость реагентов в воздухе и азоте и сделана корреляция с методом осушки. Оба 8-селенохинолин и его натриева соль могут существовать в форме моногидрата. Обнаружено что натриева соль 8-селенохинолина представляет собой самую лучшую форму реагента для весового определения; она может храниться в устоичивой форме под азотом и в сосуде содержащем силикагель.

Determination of plutonium by two-step flow-coulometry at the column electrode: SORIN KIHARA, TADASHI YAMAMOTO, KENJI MOTOJIMA and TAITIRO FUJINAGA, *Talanta*, 1972, **19**, 657. (Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan, and Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto, Japan.)

Summary—A two-step flow-coulometry method has been developed for rapid determination of elements (plutonium, iron, *etc*) which exist in various oxidation states in solution, and applied to the determination of plutonium in $0{\cdot}5M$ sulphuric acid medium. The first-step column electrode potential is fixed at between +0·10 and +0·35 V *vs.* Ag–AgCl, and all plutonium ions are reduced to Pu(III). The second-step column electrode potential is fixed at +0·75 V *vs.* Ag–AgCl, and Pu(III) which flows from the first column electrode is oxidized to Pu(IV). The quantity of plutonium is determined from the number of coulombs used in the oxidation. It is possible to eliminate interference by diverse ions by electroanalysis at the first column electrode. About a 10-μl sample is necessary and the electrolysis for determination is finished in 1 min.

Rapid analysis of fertilizers by the direct-reading thermometric method: ISTVÁN SAJÓ and B. SIPOS, *Talanta*, 1972, **19**, 669. (Research Institute for Ferrous Metallurgy, Budapest, Hungary.)

Summary—The authors have developed rapid methods for the determination of the main components of fertilizers, namely phosphate, potassium and nitrogen fixed in various forms. In the absence of magnesium ions phosphate is precipitated with magnesia mixture; in the presence of magnesium ions ammonium phosphomolybdate is precipitated and the excess of molybdate is reacted with hydrogen peroxide. Potassium is determined by precipitation with silicofluoride. For nitrogen fixed as ammonium salts the ammonium ions are condensed in a basic solution with formalin to hexamethylenetetramine; for nitrogen fixed as carbamide the latter is decomposed with sodium nitrite; for nitrogen fixed as nitrate the latter is reduced with titanium(III). In each case the temperature change of the test solution is measured. Practically all essential components of fertilizers may be determined by direct-reading thermometry; with this method and special apparatus the time of analysis is reduced to at most about 15 min for any determination.

Catalytic reactions—II. Activation: P. R. BONTCHEV, *Talanta*, 1972, **19**, 675. (Department of Analytical Chemistry, University of Sofia, 1 Anton Ivanov Str., Sofia 26, Bulgaria.)

Summary—The activation of the homogeneous catalytic reactions used in analysis is discussed. The use of activators in catalytic methods permits increase in their sensitivity by 2–4 orders of magnitude and improvement in their selectivity as well. Many different mechanisms of activation are discussed and used as illustrations of the principles for choice of an appropriate activator.

ОПРЕДЕЛЕНИЕ ПЛУТОНИЯ МЕТОДОМ ДВУСТУПЕНЧАТОЙ ПРОТОЧНОЙ КУЛОНОМЕТРИИ:

Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga, *Talanta*, 1972, **19**, 657.

Резюме—Разработан метод двуступенчатой проточной кулонометрии для быстрого определения элементов (плутония, железа и др.), существующих в различных степенях окисленния в растворе, и применен к определению плутония в растворе 0,5M серной кислоты. Потенциал электрода первой колонки установлен при +0,10 — +0,35 в в сравнении с Ag-AgCl электродом и все ионы плутония восстанавливаются до Pu(III). Потенциал электрода второй колонки установлен при +0,75 в в сравнении с Ag-AgCl электродом и вытекающие из электрода первой колонки ионы Pu(III) окисляются до Pu(IV). Концентрация плутония определена числом кулонов использованных для окисления. Метод позволяет устранять влияние разных ионов электроанализом при электроде первой колонки. Метод изыскует 10 мкл пробы а продолжительность электролиза—I мин.

БЫСТРЫЙ АНАЛИЗ УДОБРИТЕЛЕЙ МЕТОДОМ ТЕРМОМЕТРИЧЕСКОГО АНАЛИЗА С НЕПОСРЕДСТВЕННЫМ ОТСЧЁТОМ:

István Sajó and B. Sipos, *Talanta*, 1972, **19**, 669.

Резюме—Авторами разработаныбыстрые методы определения главных компонентов удобрителей, именно фосфата, калия и азота, связанных в разных соединениях. В отсутствии ионов магния фосфат осаждают магнезиальной смесью; в присутствии ионов магния осаждают фосфомолибдат аммония, а избыток молибдата реагируют перекисью водорода. Калий определяют осаждением солью кремнефтористо-водородной кислоты. Азот в форме солей аммония определяют конденсацией в основном растворе с формальдегидом в гексаметилентетрамин; для определения азота в форме карбамида, это соединение разлагают нитритом натрия; азот в форме нитрата определяют восстановлением титаном(III). В каждом определении измеряют перемены температуры исследуемого раствора. Метод термометрического анализа с непосредственным отсчетом позволяет определять почти все существенные компоненты удобрителей. Применением этого метода и специального прибора продолжительность анализа сокращается до 15 мин для каждого определения.

КАТАЛИТИЧЕСКИЕ РЕАКЦИИ—II. АКТИВАЦИЯ:

P. R. Bontchev, *Talanta*, 1972, **19**, 675.

Резюме—Рассмотрена активация гомогенных каталитических реакций, применимых в анализе. Использование активаторов в каталитических методах позволяет повышать в 2 — 4 раз их чувствительность а также улучшать их избирательность. Рассмотрены разные механизмы активации и на их основе объяснены принципы отбора подходящего активатора.

N-Acetylacetone–anthranilic acid as a gravimetric reagent for copper(II): R. K. MEHTA, R. K. GUPTA and S. L. PANIA, *Talanta*, 1972, **19**, 687. (Department of Chemistry, University of Jodhpur, Jodhpur, India.)

Summary—*N*-Acetylacetone–anthranilic acid has been employed as a reagent for the gravimetric determination of copper(II). The solid copper(II) chelate formed possesses 1:1 metal–ligand stoichiometry and is found to exist as an unsolvated dimer. The complex has a magnetic moment of 1·88 B.M. at 298 K. A non-planar dimeric structure is suggested to explain the observed facts.

Analysis of metals by solid–liquid separation after liquid–liquid extraction. Spectrophotometric determination of palladium(II) by extraction of palladium dimethylglyoximate with melted naphthalene: TAITIRO FUJINAGA, MASATADA SATAKE and TATSUO YONEKUBO, *Talanta*, 1972, **19**, 689. (Faculty of Science, Kyoto University, Sakyo-ku, Kyoto-shi, Japan, and Faculty of Engineering, Fukui University, Fukui-shi, Japan.)

Summary—A method of liquid–liquid extraction of palladium dimethylglyoximate with molten naphthalene followed by solid–liquid separation is successfully applied to palladium. The complex between palladium and dimethylglyoxime is easily extracted into molten naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1 \cdot 72 \times 10^4$ l.mole.$^{-1}$mm^{-1}. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Détermination gravimétrique de l'iode sous forme de Nt(ICl$_2$): N. GANTCHEV, V. KANAZIRSKA and D. ATHANASSOVA, *Talanta*, 1972, **19**, 692. (Chaire de chimie analytique, Ecole Normale Supérieure, 7 rue "V. Markov", Plovdiv, Bulgarie.)

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

N-АЦЕТИЛАЦЕТОНАНТРАНИЛОВАЯ КИСЛОТА В КАЧЕСТВЕ ВЕСОВОГО РЕАГЕНТА ДЛЯ МЕДИ(II):

R. K. Mehta, R. K. Gupta and S. L. Pania, *Talanta*, 1972, **19**, 687.

Резюме—N-Ацетилацетонантраниловая кислота использована в качестве реагента для весового определения меди(II). Образующийся твёрдый хелат меди(II) представляет собой 1:1 металл-лиганд комплекс и существует в форме несольватизированного димера. Магнитный момент комплекса равен 1,88 Б.М. при 298°К. Обнаруженные свойства объясняются непланарной димерной структурой комплекса.

АНАЛИЗ МЕТАЛЛОВ МЕТОДОМ РАЗДЕЛЕНИЯ ТВЁРДОЙ И ЖИДКОЙ ФАЗ ПОСЛЕ ЖИДКОФАЗНОЙ ЭКСТРАКЦИИ:—СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ(II) ЭКСТРАГИРОВАНИЕМ ДИМЕТИЛГЛИОКСИМАТА ПАЛЛАДИЯ РАСПЛАВЛЕННЫМ НАФТАЛИНОМ:

Taitiro Fujinaga, Masatada Satake and Tatsuo Yonekubo, *Talanta*, 1972, **19**, 689.

Резюме—Метод жидкофазной экстракции диметилглиоксимата паллация расплавленным нафталином с последующим разделением твёрдой и жидкой фаз успешно применен в определении палладия. Комплекс диметилглиоксима с палладием легко экстрагируется расплавленным нафталином. После экстракции весьма мелкие кристаллы нафталина растворяют в хлороформе и измеряют светопоглощение полученного раствора при 370 нм в сравнении с слепой пробой реагента. Закон Бера почитается в области 30 – 370 мкг палладия в 10 мл хлороформа, а молярное поглощение $-1,72 \times 10^4$.л. моль$^{-1}$.мм$^{-1}$. Разные соли щелочных металлов не мешают определению. Влияние никеля(II) устраняется экстрагированием при pH 2, а влияние железа(III)—маскированием с ЭДТА или восстановлением до железа(II). Метод является быстрым и точным.

ГРАВИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИОДА В ФОРМЕ $Nt(ICl_2)$:

N. Gantchev, V. Kanazirska and D. Athanassova, *Talanta*, 1972, **19**, 692.

Резюме—Приготовлен и изучен нитрон-дихлориодид $Nt(ICl_2)$ и использован в качестве реагента для гравиметрического определения иода. В области 4 – 40 мг иода ошибка меньше чем в определении в форме A I. Бромат и хлорат не мешают определению.

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten: H. Kroschwitz, E. Pungor and S. Ferenczi, *Talanta*, 1972, **19**, 695. (Institut für Allgemeine und Analytische Chemie, Technische Universität, Budapest XI, Gellért tér 4, Hungary, and Institut für Biochemie der Ungarischen Akademie der Wissenschaften Budapest XI, Karolina út 29–31.)

Summary—A procedure is described for the separation of mono-, di- and triphosphate, and of monophosphate and mono-, di- and triamidophosphate on ready-made thin-layer plates of anion-exchange resin Dowex 2-X8. The procedure couples the advantages of thin-layer chromatography with those of ion-exchange techniques. By suitable choice of anion for the resin (*i.e.*, chloride or acetate) only one stock buffer solution is needed for the separation. The two classes of compounds do not interfere with each other during the separations.

Potentiometric determination of stepwise stability constants of zirconium and thorium chelates formed with aspartic and glutamic acids: M. K. Singh and M. N. Srivastava, *Talanta*, 1972, **19**, 699. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in $0.1M$ sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Thermodynamic association constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid: Y. K. Agrawal and S. G. Tandon, *Talanta*, 1972, **19**, 700. (Department of Chemistry, Govt. Science College, Raipur (M.P.), India.)

Summary—Thermodynamic association constants of benzohydroxamic acid and several *ortho*-substituted *N*-phenylbenzohydroxamic acids have been determined by pH titration in aqueous dioxan media at 25° and 35°. Empirical pH corrections for mixed aqueous media have been applied. The pK_a values do not vary linearly with the reciprocal of dielectric constant of the medium, but a plot of pK_a *vs.* the mole fraction of dioxan is linear at a given temperature. Values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are tabulated.

РАЗДЕЛЕНИЕ НЕОРГАНИЧЕСКИХ ФОСФАТОВ МЕТОДОМ ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ НА КОММЕРЧЕСКИХ СЛОЯХ АНИОНООБМЕННИКОВ:

H. Kroschwitz, E. Pungor and S. Ferenczi, *Talanta*, 1972, **19**, 695.

Резюме—Описана методика разделения моно-, ди- и трифосфата, монофосфата и моно-, ди- и трамидофосфата на коммерческих пластинках для тонкослойной хроматографии на слоях анионообменной смолы Дауекс 2-X8. Метод объединяет преимущества тонкослойной хроматографии с преимуществами ионного обмена. Подходящии отбор аниона смолы (на пр. хлорида или ацетата) позволяет провести разделение только с одним буферным раствором. Два класса соединений не влияют один на другого в этих соединениях.

СТУПЕНЧАТОЕ ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОНСТАНТ УСТОИЧИВОСТИ ХЕЛАТОВ ЦИРКОНИЯ И ТОРИЯ С АСПАРАГИНОВОЙ И ГЛУТАМИНОВОЙ КИСЛОТАМИ:

M. K. Singh and M. N. Srivastava, *Talanta*, 1972, **19**, 699.

Резюме—Исследованы потенциометрическим методом хелаты Zr(IV) и Th(IV) с аспарагиновой и глутаминовой кислотами. Определены следующие константы устойчивости в 0,1*M* перхлорате натрия при 25°: хелаты аспарагиновой кислоты—$\lg K_1$ 9,70, $\lg K_2$ 6,85, $\lg K_3$ 3,50 для Zr и $\lg K_1$ 9,23, $\lg K_2$ 8,57, $\lg K_3$ 4,55, $\lg K_4$ 3,87 для Th; хелаты глутаминовой кислоты—$\lg K_1$ 9,60, $\lg K_2$ 6,40, $\lg K_3$ 3,32 для Zr и $\lg K_1$ 9,11, $\lg K_2$ 8,52, $\lg K_3$ 4,18, $\lg K_4$ 3,62 для Th.

ТЕРМОДИНАМИЧЕСКИЕ КОНСТАНТЫ АССОЦИАЦИИ *N*-ФЕНИЛБЕНЗГИДРОКСАМОВЫХ КИСЛОТ И БЕНЗГИДРОКСАМОВОЙ КИСЛОТЫ:

Y. K. Agrawal and S. G. Tandon, *Talanta*, 1972, **19**, 700.

Резюме—Определены методом титрования pH термодинамические константы ассоциации бензгидроксамовой кислоты и некоторых орто-замещенных *N*-фенилбензгидроксамовых кислот в водных растворах диоксана при 25° и 35°. Применены эмпирические поправки для смешанных водных сред. Величины pK_a не показывают линейную зависымость от обратной величины диэлектнрической постоянной среды, но pK_a в зависимости от мольной доли диоксана представляет собой прямолинейную функцию для данной температуры. Приведены таблицы величин $\Delta G°$, $\Delta H°$ и $\Delta S°$.

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions: P. C. RAWAT and C. M. GUPTA, *Talanta*, 1972, **19**, 706. (Department of Chemistry, M.R.E. College, Jaipur-4, India and Chemical Laboratories, University of Rajasthan, Jaipur-4, India.)

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water-methanol solutions at 30 ± 0.1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in $0.01M$ HCl, with $0.1M$ KCl as supporting electrolyte.

Determination of pK_a of acetic and benzoic acids in pyridine: L. M. MUKHERJEE and RONALD S. SCHULTZ, *Talanta*, 1972, **19**, 708. (Chemistry Department, Illinois State University, Normal, Ill. 61761, U.S.A.)

Summary—The pK_a's of acetic acid and benzoic acid in pyridine as solvent are found to be 10·1 and 9·8, respectively, at 25°. These results are based on measurements of hydrogen ion activities in mixtures of the acids and their tetrabutylammonium salts. Supplementary studies of differential vapour pressure characteristics of solutions of the acids and the acid-salt mixtures, and conductance of tetrabutylammonium benzoate solutions are also incorporated.

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions: J. P. SHUKLA and S. G. TANDON, *Talanta*, 1972, **19**, 711. (Department of Chemistry, Government College of Science, Raipur, M.P., India.)

Summary—Thermodynamic stability constants of complexes of Mn(II), Ni(II), Zn(II) and Cu(II) with five closely related *N*-arylhydroxamic acids have been determined at 25 ± 0·1° in 50% v/v aqueous dioxan medium. The stabilities of the complexes mostly follow the order of the basicity of the ligands and the electron affinities of the metal ions as measured by their second ionization potential.

ХАРАКТЕРИСТИКИ КОМПЛЕКСОВ ИНДИЯ(III) И УРАНА(VI) С ТИОДИПРОПИОНОВОЙ КИСЛОТОЙ НА КАПЕЛЬНОМ РТУТНОМ ЭЛЕКТРОДЕ В ВОДНЫХ И ВОДНО-МЕТАНОЛОВЫХ РАСТВОРАХ:

P. C. Rawat and C. M. Gupta, *Talanta*, 1972, **19**, 706.

Резюме—Комплексообразование In(III) и U(VI) с тиодипропионовой кислотой изучено полярографическим методом в водных и водно-метаноловых растворах при 30 ± 0,1°. Все хелаты относятся к полярографически обратимыми системами. В случае индия(III) образуются при pH 4,8 комплексы имеющие отношения металля к лиганду 1:1, 1:2, 1:3 и 1:4. В случае урана(VI) образуются три последовательных комплекса имеющие отношения металла к лиганду 1:1, 1:2 и 1:3 в 0,01*M* HCl, с использованием 0,1*M* KCl в качестве фона.

ОПРЕДЕЛЕНИЕ pK_a УКСУСНОЙ И БЕНЗОЙНОЙ КИСЛОТ В ПИРИДИНЕ:

L. M. Mukherjee and Ronald S. Schultz, *Talanta*, 1972, **19**, 708.

Резюме—pK_a уксусной и бензойной кислот в пиридине в качестве растворителя равны 10,1 и 9,8, соответственно, при 25°. Эти результаты основаны на измерении активности ионов водорода в смесях кислот и их солей тетрабутиламмония. Также приведены результаты изучения дифференциальной упругости паров растворов этих кислот и их смесей с солями и проводимости растворов бензоата тетрабутиламмония.

КОНСТАНТЫ УСТОЙЧИВОСТИ КОМПЛЕКСОВ *N*-АРИЛГИДРОКСАМОВЫХ КИСЛОТ С НЕКОТОРЫМИ ДВУВАЛЕНТНЫМИ ИОНАМИ МЕТАЛЛОВ:

J. P. Shukla and S. G. Tandon, *Talanta*, 1972, **19**, 711.

Резюме—Определены термодинамические константы устойчивости комплексов Mn(II), Ni(II), Zn(II) и Cu(II) и пять узкосвязанных *N*-арилгидроксамовых кислот при 25 ± 0,1° в 50%-тном водном растворе диоксана. Устойчивость кмплексов в большинстве случаев следует порядок основности лигандов и электронное сродство ионов металлов, приказанное их вторим ионизационным напряжением.

SUMMARIES FOR CARD INDEXES

Analytical mass spectrometry: J. R. MAJER, *Talanta*, 1972, **19**, 589. (Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham 15, U.K.)

Summary—A review is made of the basic theory, instrumentation and application of mass spectrometry, with special reference to the development of the equipment and its impact on the scope of application.

Development and publication of work with selective ion-sensitive electrodes: G. J. MOODY and J. D. R. THOMAS, *Talanta*, 1972, **19**, 623. (University of Wales Institute of Science and Technology, Cardiff, Wales.)

Summary—Features concerning development, response, selectivity and applications of selective ion-sensitive electrodes are reviewed. Recommendations are made concerning investigations involving the development and applications of electrodes and attention given to the manner of presenting data for publication.

Iodometric microdetermination of sulphur in organic compounds by an amplification method: Y. A. GAWARGIOUS and A. B. FARAG, *Talanta*, 1972, **19**, 641. (Microanalytical Research Laboratory, National Research Centre, Dokki, Cairo, U.A.R.)

Summary—A new method is described for the iodometric microdetermination of sulphur in organic compounds, using a 12-fold amplification reaction after oxygen-flask combustion. The method is based on reaction of the resulting sulphuric acid with an excess of saturated barium bromate solution. The unreacted barium bromate is precipitated by addition of acetone, filtered off, redissolved in hot water and after addition of an excess of iodide and acid, the iodine liberated is titrated with thiosulphate. The method is simple, rapid, highly accurate, and of wide application in the microanalysis of organosulphur compounds containing other common acid-forming elements.

Improved synthesis and stability of 8-selenoquinoline and its sodium salt as organic reagents: EIICHI SEKIDO and ISAMU FUJIWARA, *Talanta*, 1972, **19**, 647. (Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe, Japan).

Summary—The synthesis of 8-selenoquinoline and its sodium salt has been improved by optimization of each process. The stability of the reagents in air and nitrogen has been examined and correlated with the drying method. Both 8-selenoquinoline and its sodium salt can exist as the monohydrate. It was found that the sodium salt of 8-selenoquinoline monohydrate is best as the weighing form of the reagent and that it can be kept stable under nitrogen in a vessel containing silica gel.

МАСС-СПЕКТРОМЕТРИЯ В АНАЛИЗЕ:

J. R. Majer, *Talanta*, 1972, **19**, 589.

Резюме—Приведен обзор основной теории, прибора и применения масс-спектрометрии, с особым учетом разработки аппаратуры и его эффекта на область применения метода.

РАЗРАБОТКА И ОПУБЛИКОВАНИЕ РАБОТ ПОЛЬЗУЮЩИСЯ ИОНОИЗБИРАТЕЛЬНЫМИ ЭЛЕКТРОДАМИ:

G. J. Moody and J. D. R. Thomas, *Talanta*, 1972, **19**, 623.

Резюме—Приведен обзор разработки, ответа, избирательности и применения ионоизбирательных электродов. Предложены исследования в области разработки и применения электродов и указаны пути приведения данных в статях.

МИКРОМЕТОД ИОДОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ СЕРЫ В ОРГАНИЧЕСКИХ СОЕДИНЕНИЯХ С ИСПОЛЬЗОВАНИЕМ АМПЛИФИКАЦИИ:

Y. A. Gawargious and A. B. Farag, *Talanta*, 1972, **19**, 641.

Резюме—Описан новый микрометод для иодометрического определения серы в органических соединениях, пользующийся 12-кратной амплификационной реакцией после сожжения в кольбе, наполненной кислородом. Метод основан на реакции образующейся серной кислоты с избытком насыщенного раствора бромата бария. Нереагированный бромат бария осаждают добавлением ацетона, фильтрируют, осадок растворяют в кипящей воде и—после добавления избытка иодида и кислоты—выделенный иод титрируют раствором тиосульфата. Метод оказался несложным, быстрым и весьма точным; он широко применим в микроанализе органических соединений серы, содержащих другие обыкновенные образующие кислоты элементы.

УЛУЧШЕННЫЙ СИНТЕЗ И СТАБИЛЬНОСТЬ 8-СЕЛЕНОХИНОЛИНА И ЕГО НАТРИЕВОЙ СОЛИ В КАЧЕСТВЕ ОРГАНИЧЕСКИХ РЕАГЕНТОВ:

Eiichi Sekido and Isamu Fujiwara, *Talanta*, 1972, **19**, 647.

Резюме—Синтез 8-селенохинолина и его натриевой соли улучшен путем оптимизации каждого процесса. Испытана устоичивость реагентов в воздухе и азоте и сделана корреляция с методом осушки. Оба 8-селенохинолин и его натриева соль могут существовать в форме моногидрата. Обнаружено что натриева соль 8-селенохинолина представляет собой самую лучшую форму реагента для весового определения; она может храниться в устоичивой форме под азотом и в сосуде содержащем силикагель.

Determination of plutonium by two-step flow-coulometry at the column electrode: SORIN KIHARA, TADASHI YAMAMOTO, KENJI MOTOJIMA and TAITIRO FUJINAGA, *Talanta*, 1972, **19**, 657. (Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan, and Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto, Japan.)

Summary—A two-step flow-coulometry method has been developed for rapid determination of elements (plutonium, iron, *etc*) which exist in various oxidation states in solution, and applied to the determination of plutonium in $0{\cdot}5M$ sulphuric acid medium. The first-step column electrode potential is fixed at between $+0{\cdot}10$ and $+0{\cdot}35$ V *vs.* Ag–AgCl, and all plutonium ions are reduced to Pu(III). The second-step column electrode potential is fixed at $+0{\cdot}75$ V *vs.* Ag–AgCl, and Pu(III) which flows from the first column electrode is oxidized to Pu(IV). The quantity of plutonium is determined from the number of coulombs used in the oxidation. It is possible to eliminate interference by diverse ions by electroanalysis at the first column electrode. About a 10-μl sample is necessary and the electrolysis for determination is finished in 1 min.

Rapid analysis of fertilizers by the direct-reading thermometric method: ISTVÁN SAJÓ and B. SIPOS, *Talanta*, 1972, **19**, 669. (Research Institute for Ferrous Metallurgy, Budapest, Hungary.)

Summary—The authors have developed rapid methods for the determination of the main components of fertilizers, namely phosphate, potassium and nitrogen fixed in various forms. In the absence of magnesium ions phosphate is precipitated with magnesia mixture; in the presence of magnesium ions ammonium phosphomolybdate is precipitated and the excess of molybdate is reacted with hydrogen peroxide. Potassium is determined by precipitation with silicofluoride. For nitrogen fixed as ammonium salts the ammonium ions are condensed in a basic solution with formalin to hexamethylenetetramine; for nitrogen fixed as carbamide the latter is decomposed with sodium nitrite; for nitrogen fixed as nitrate the latter is reduced with titanium(III). In each case the temperature change of the test solution is measured. Practically all essential components of fertilizers may be determined by direct-reading thermometry; with this method and special apparatus the time of analysis is reduced to at most about 15 min for any determination.

Catalytic reactions—II. Activation: P. R. BONTCHEV, *Talanta*, 1972, **19**, 675. (Department of Analytical Chemistry, University of Sofia, 1 Anton Ivanov Str., Sofia 26, Bulgaria.)

Summary—The activation of the homogeneous catalytic reactions used in analysis is discussed. The use of activators in catalytic methods permits increase in their sensitivity by 2–4 orders of magnitude and improvement in their selectivity as well. Many different mechanisms of activation are discussed and used as illustrations of the principles for choice of an appropriate activator.

ОПРЕДЕЛЕНИЕ ПЛУТОНИЯ МЕТОДОМ ДВУСТУПЕНЧАТОЙ ПРОТОЧНОЙ КУЛОНОМЕТРИИ:

Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga, *Talanta*, 1972, **19**, 657.

Резюме—Разработан метод двуступенчатой проточной кулонометрии для быстрого определения элементов (плутония, железа и др.), существующих в различных степенях окисленния в растворе, и применен к определению плутония в растворе 0,5*M* серной кислоты. Потенциал электрода первой колонки установлен при +0,10 — +0,35 в в сравнении с Ag-AgCl электродом и все ионы плутония восстанавливаются до Pu(III). Потенциал электрода второй колонки установлен при +0,75 в в сравнении с Ag-AgCl электродом и вытекающие из электрода первой колонки ионы Pu(III) окисляются до Pu(IV). Концентрация плутония определена числом кулонов использованных для окисления. Метод позволяет устранять влияние разных ионов электроанализом при электроде первой колонки. Метод изыскует 10 мкл пробы а продолжительность электролиза—I мин.

БЫСТРЫЙ АНАЛИЗ УДОБРИТЕЛЕЙ МЕТОДОМ ТЕРМОМЕТРИЧЕСКОГО АНАЛИЗА С НЕПОСРЕДСТВЕННЫМ ОТСЧЁТОМ:

István Sajó and B. Sipos, *Talanta*, 1972, **19**, 669.

Резюме—Авторами разработаныбыстрые методы определения главных компонентов удобрителей, именно фосфата, калия и азота, связанных в разных соединениях. В отсутствии ионов магния фосфат осаждают магнезиальной смесью; в присутствии ионов магния осаждают фосфомолибдат аммония, а избыток молибдата реагируют перекисью водорода. Калий определяют осаждением солью кремнефтористо-водородной кислоты. Азот в форме солей аммония определяют конденсацией в основном растворе с формальдегидом в гексаметилентетрамин; для определения азота в форме карбамида, это соединение разлагают нитритом натрия; азот в форме нитрата определяют восстановлением титаном(III). В каждом определении измеряют перемены температуры исследуемого раствора. Метод термометрического анализа с непосредственным отсчетом позволяет определять почти все существенные компоненты удобрителей. Применением этого метода и специального прибора продолжительность анализа сокращается до 15 мин для каждого определения.

КАТАЛИТИЧЕСКИЕ РЕАКЦИИ—II. АКТИВАЦИЯ:

P. R. Bontchev, *Talanta*, 1972, **19**, 675.

Резюме—Рассмотрена активация гомогенных каталитических реакций, применимых в анализе. Использование активаторов в каталитических методах позволяет повышать в 2 — 4 раз их чувствительность а также улучшать их избирательность. Рассмотрены разные механизмы активации и на их основе объяснены принципы отбора подходящего активатора.

N-Acetylacetone–anthranilic acid as a gravimetric reagent for copper(II): R. K. Mehta, R. K. Gupta and S. L. Pania, *Talanta*, 1972, **19**, 687. (Department of Chemistry, University of Jodhpur, Jodhpur, India.)

Summary—*N*-Acetylacetone–anthranilic acid has been employed as a reagent for the gravimetric determination of copper(II). The solid copper(II) chelate formed possesses 1:1 metal–ligand stoichiometry and is found to exist as an unsolvated dimer. The complex has a magnetic moment of 1·88 B.M. at 298 K. A non-planar dimeric structure is suggested to explain the observed facts.

Analysis of metals by solid–liquid separation after liquid–liquid extraction. Spectrophotometric determination of palladium(II) by extraction of palladium dimethylglyoximate with melted naphthalene: Taitiro Fujinaga, Masatada Satake and Tatsuo Yonekubo, *Talanta*, 1972, **19**, 689. (Faculty of Science, Kyoto University, Sakyo-ku, Kyoto-shi, Japan, and Faculty of Engineering, Fukui University, Fukui-shi, Japan.)

Summary—A method of liquid–liquid extraction of palladium dimethylglyoximate with molten naphthalene followed by solid–liquid separation is successfully applied to palladium. The complex between palladium and dimethylglyoxime is easily extracted into molten naphthalene. After extraction, the very fine solidified naphthalene crystals are dissolved in chloroform, and the absorbance of the resultant solution is measured at 370 nm against a reagent blank. Beer's law is obeyed for 30–370 μg of palladium in 10 ml of chloroform, and the molar absorptivity is calculated to be $1 \cdot 72 \times 10^4$ $l.mole.^{-1}mm^{-1}$. Various alkali metal salts and metal ions do not interfere. The interference of nickel(II) is overcome by the extraction at pH 2, and that of iron(III) by masking with EDTA or by reduction to iron(II). The method is rapid and accurate.

Détermination gravimétrique de l'iode sous forme de Nt(ICl$_2$): N. Gantchev, V. Kanazirska and D. Athanassova, *Talanta*, 1972, **19**, 692. (Chaire de chimie analytique, Ecole Normale Supérieure, 7 rue "V. Markov", Plovdiv, Bulgarie.)

Summary—Nitron dichloroiodide—Nt(ICl$_2$)—has been prepared and studied, and a gravimetric determination of iodine as Nt(ICl)$_2$ has been based on the result. For 4–40 mg of iodine the error is less than that of the determination as AgI. Bromate and chlorate do not interfere.

N-АЦЕТИЛАЦЕТОНАНТРАНИЛОВАЯ КИСЛОТА В КАЧЕСТВЕ ВЕСОВОГО РЕАГЕНТА ДЛЯ МЕДИ(II):

R. K. Mehta, R. K. Gupta and S. L. Pania, *Talanta*, 1972, **19**, 687.

Резюме—*N*-Ацетилацетонантраниловая кислота использована в качестве реагента для весового определения меди(II). Образующийся твёрдый хелат меди(II) представляет собой 1:1 металл-лиганд комплекс и существует в форме несольватизированного димера. Магнитный момент комплекса равен 1,88 Б.М. при 298°К. Обнаруженные свойства объясняются непланарной димерной структурой комплекса.

АНАЛИЗ МЕТАЛЛОВ МЕТОДОМ РАЗДЕЛЕНИЯ ТВЁРДОЙ И ЖИДКОЙ ФАЗ ПОСЛЕ ЖИДКОФАЗНОЙ ЭКСТРАКЦИИ:—СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ(II) ЭКСТРАГИРОВАНИЕМ ДИМЕТИЛГЛИОКСИМАТА ПАЛЛАДИЯ РАСПЛАВЛЕННЫМ НАФТАЛИНОМ:

Taitiro Fujinaga, Masatada Satake and Tatsuo Yonekubo, *Talanta*, 1972, **19**, 689.

Резюме—Метод жидкофазной экстракции диметилглиоксимата паллация расплавленным нафталином с последующим разделением твёрдой и жидкой фаз успешно применен в определении палладия. Комплекс диметилглиоксима с палладием легко экстрагируется расплавленным нафталином. После экстракции весьма мелкие кристаллы нафталина растворяют в хлороформе и измеряют светопоглощение полученного раствора при 370 нм в сравнении с слепой пробой реагента. Закон Бера почитается в области 30 – 370 мкг палладия в 10 мл хлороформа, а молярное поглощение $-1{,}72 \times 10^4$.л. моль$^{-1}$.мм$^{-1}$. Разные соли щелочных металлов не мешают определению. Влияние никеля(II) устраняется экстрагированием при pH 2, а влияние железа(III)—маскированием с ЭДТА или восстановлением до железа(II). Метод является быстрым и точным.

ГРАВИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ИОДА В ФОРМЕ $Nt(ICl_2)$:

N. Gantchev, V. Kanazirska and D. Athanassova, *Talanta*, 1972, **19**, 692.

Резюме—Приготовлен и изучен нитрон-дихлориодид $Nt(ICl_2)$ и использован в качестве реагента для гравиметрического определения иода. В области 4 – 40 мг иода ошибка меньше чем в определении в форме A I. Бромат и хлорат не мешают определению.

Trennung anorganischer Phosphate an Anionenaustauscher-Fertigplatten: H. Kroschwitz, E. Pungor and S. Ferenczi, *Talanta*, 1972, **19**, 695. (Institut für Allgemeine und Analytische Chemie, Technische Universität, Budapest XI, Gellért tér 4, Hungary, and Institut für Biochemie der Ungarischen Akademie der Wissenschaften Budapest XI, Karolina út 29–31.)

Summary—A procedure is described for the separation of mono-, di- and triphosphate, and of monophosphate and mono-, di- and triamidophosphate on ready-made thin-layer plates of anion-exchange resin Dowex 2-X8. The procedure couples the advantages of thin-layer chromatography with those of ion-exchange techniques. By suitable choice of anion for the resin (*i.e.*, chloride or acetate) only one stock buffer solution is needed for the separation. The two classes of compounds do not interfere with each other during the separations.

Potentiometric determination of stepwise stability constants of zirconium and thorium chelates formed with aspartic and glutamic acids: M. K. Singh and M. N. Srivastava, *Talanta*, 1972, **19**, 699. (Chemical Laboratories, University of Allahabad, Allahabad, India.)

Summary—The metal chelates of Zr(IV) and Th(IV) with aspartic and glutamic acids have been studied potentiometrically. Stepwise stability constants in 0.1*M* sodium perchlorate at 25° are reported as: aspartate chelates—log K_1 9·70, log K_2 6·85, and log K_3 3·50 for Zr, and log K_1 9·23, log K_2 8·57, log K_3 4·55 and log K_4 3·87 for Th; glutamate chelates—log K_1 9·60, log K_2 6·40 and log K_3 3·32 for Zr and log K_1 9·11, log K_2 8·52, log K_3 4·18 and log K_4 3·62 for Th.

Thermodynamic association constants of *N*-phenylbenzohydroxamic acids and benzohydroxamic acid: Y. K. Agrawal and S. G. Tandon, *Talanta*, 1972, **19**, 700. (Department of Chemistry, Govt. Science College, Raipur (M.P.), India.)

Summary—Thermodynamic association constants of benzohydroxamic acid and several *ortho*-substituted *N*-phenylbenzohydroxamic acids have been determined by pH titration in aqueous dioxan media at 25° and 35°. Empirical pH corrections for mixed aqueous media have been applied. The pK_a values do not vary linearly with the reciprocal of dielectric constant of the medium, but a plot of pK_a *vs.* the mole fraction of dioxan is linear at a given temperature. Values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are tabulated.

РАЗДЕЛЕНИЕ НЕОРГАНИЧЕСКИХ ФОСФАТОВ МЕТОДОМ ТОНКОСЛОЙНОЙ ХРОМАТОГРАФИИ НА КОММЕРЧЕСКИХ СЛОЯХ АНИОНООБМЕННИКОВ:

H. Kroschwitz, E. Pungor and S. Ferenczi, *Talanta*, 1972, **19**, 695.

Резюме—Описана методика разделения моно-, ди- и трифосфата, монофосфата и моно-, ди- и трамидофосфата на коммерческих пластинках для тонкослойной хроматографии на слоях анионообменной смолы Дауекс 2-Х8. Метод объединяет преимущества тонкослойной хроматографии с преимуществами ионного обмена. Подходящии отбор аниона смолы (на пр. хлорида или ацетата) позволяет провести разделение только с одним буферным раствором. Два класса соединений не влияют один на другого в этих соединениях.

СТУПЕНЧАТОЕ ПОТЕНЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ КОНСТАНТ УСТОИЧИВОСТИ ХЕЛАТОВ ЦИРКОНИЯ И ТОРИЯ С АСПАРАГИНОВОЙ И ГЛУТАМИНОВОЙ КИСЛОТАМИ:

M. K. Singh and M. N. Srivastava, *Talanta*, 1972, **19**, 699.

Резюме—Исследованы потенциометрическим методом хелаты Zr(IV) и Th(IV) с аспарагиновой и глутаминовой кислотами. Определены следующие константы устойчивости в 0,1*M* перхлорате натрия при 25°: хелаты аспарагиновой кислоты—lg K_1 9,70, lg K_2 6,85, lg K_3 3,50 для Zr и lg K_1 9,23, lg K_2 8,57, lg K_3 4,55, lg K_4 3,87 для Th; хелаты глутаминовой кислоты—lg K_1 9,60, lg K_2 6,40, lg K_3 3,32 для Zr и lg K_1 9,11, lg K_2 8,52, lg K_3 4,18, lg K_4 3,62 для Th.

ТЕРМОДИНАМИЧЕСКИЕ КОНСТАНТЫ АССОЦИАЦИИ *N*-ФЕНИЛБЕНЗГИДРОКСАМОВЫХ КИСЛОТ И БЕНЗГИДРОКСАМОВОЙ КИСЛОТЫ:

Y. K. Agrawal and S. G. Tandon, *Talanta*, 1972, **19**, 700.

Резюме—Определены методом титрования pH термодинамические константы ассоциации бензгидроксамовой кислоты и некоторых орто-замещенных *N*-фенилбензгидроксамовых кислот в водных растворах диоксана при 25° и 35°. Применены эмпирические поправки для смешанных водных сред. Величины pK_a не показывают линейную зависимость от обратной величины диэлектнрической постоянной среды, но pK_a в зависимости от мольной доли диоксана представляет собой прямолинейную функцию для данной температуры. Приведены таблицы величин $\Delta G°$, $\Delta H°$ и $\Delta S°$.

Behaviour of the thiodipropionic complex of In(III) and U(VI) at the DME in aqueous and aqueous methanolic solutions: P. C. Rawat and C. M. Gupta, *Talanta*, 1972, **19**, 706. (Department of Chemistry, M.R.E. College, Jaipur-4, India and Chemical Laboratories, University of Rajasthan, Jaipur-4, India.)

Summary—The complexation of In(III) and U(VI) with thiodipropionic acid has been investigated polarographically in water and water-methanol solutions at 30 ± 0.1°. All the chelates belong to polarographically reversible systems. With indium(III), complexes with metal to ligand ratios of 1:1, 1:2, 1:3 and 1:4 are found at pH 4.8. Uranium(VI) is found to form three successive complexes with metal to ligand ratios of 1:1, 1:2 and 1:3 in $0.01M$ HCl, with $0.1M$ KCl as supporting electrolyte.

Determination of pK_a of acetic and benzoic acids in pyridine: L. M. Mukherjee and Ronald S. Schultz, *Talanta*, 1972, **19**, 708. (Chemistry Department, Illinois State University, Normal, Ill. 61761, U.S.A.)

Summary—The pK_a's of acetic acid and benzoic acid in pyridine as solvent are found to be 10·1 and 9·8, respectively, at 25°. These results are based on measurements of hydrogen ion activities in mixtures of the acids and their tetrabutylammonium salts. Supplementary studies of differential vapour pressure characteristics of solutions of the acids and the acid-salt mixtures, and conductance of tetrabutylammonium benzoate solutions are also incorporated.

Stability constants of complexes of *N*-arylhydroxamic acids with some bivalent metal ions: J. P. Shukla and S. G. Tandon, *Talanta*, 1972, **19**, 711. (Department of Chemistry, Government College of Science, Raipur, M.P., India.)

Summary—Thermodynamic stability constants of complexes of Mn(II), Ni(II), Zn(II) and Cu(II) with five closely related *N*-arylhydroxamic acids have been determined at 25 ± 0·1° in 50% v/v aqueous dioxan medium. The stabilities of the complexes mostly follow the order of the basicity of the ligands and the electron affinities of the metal ions as measured by their second ionization potential.

ХАРАКТЕРИСТИКИ КОМПЛЕКСОВ ИНДИЯ(III) И УРАНА(VI) С ТИОДИПРОПИОНОВОЙ КИСЛОТОЙ НА КАПЕЛЬНОМ РТУТНОМ ЭЛЕКТРОДЕ В ВОДНЫХ И ВОДНО-МЕТАНОЛОВЫХ РАСТВОРАХ:

P. C. Rawat and C. M. Gupta, *Talanta*, 1972, **19**, 706.

Резюме—Комплексообразование In(III) и U(VI) с тиодипропионовой кислотой изучено полярографическим методом в водных и водно-метаноловых растворах при 30 ± 0,1°. Все хелаты относятся к полярографически обратимыми системами. В случае индия(III) образуются при pH 4,8 комплексы имеющие отношения металля к лиганду 1:1, 1:2, 1:3 и 1:4. В случае урана(VI) образуются три последовательных комплекса имеющие отношения металла к лиганду 1:1, 1:2 и 1:3 в 0,01*M* HCl, с использованием 0,1*M* KCl в качестве фона.

ОПРЕДЕЛЕНИЕ pK_a УКСУСНОЙ И БЕНЗОЙНОЙ КИСЛОТ В ПИРИДИНЕ:

L. M. Mukherjee and Ronald S. Schultz, *Talanta*, 1972, **19**, 708.

Резюме—pK_a уксусной и бензойной кислот в пиридине в качестве растворителя равны 10,1 и 9,8, соответственно, при 25°. Эти результаты основаны на измерении активности ионов водорода в смесях кислот и их солей тетрабутиламмония. Также приведены результаты изучения дифференциальной упругости паров растворов этих кислот и их смесей с солями и проводимости растворов бензоата тетрабутиламмония.

КОНСТАНТЫ УСТОЙЧИВОСТИ КОМПЛЕКСОВ *N*-АРИЛГИДРОКСАМОВЫХ КИСЛОТ С НЕКОТОРЫМИ ДВУВАЛЕНТНЫМИ ИОНАМИ МЕТАЛЛОВ:

J. P. Shukla and S. G. Tandon, *Talanta*, 1972, **19**, 711.

Резюме—Определены термодинамические константы устойчивости комплексов Mn(II), Ni(II), Zn(II) и Cu(II) и пять узкосвязанных *N*-арилгидроксамовых кислот при 25 ± 0,1° в 50%-тном водном растворе диоксана. Устойчивость кмплексов в большинстве случаев следует порядок основности лигандов и электронное сродство ионов металлов, приказанное их вторим ионизационным напряжением.

SUMMARIES FOR CARD INDEXES

Synthetic inorganic ion-exchangers—I. Hydrous oxides and acidic salts of multivalent metals: V. Veselý and V. Pekárek, *Talanta*, 1972, **19**, 219. (Nuclear Research Institute of the Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia.)

Summary—An exhaustive literature survey is given of the hydrous oxides and acidic salts of multivalent metals that are used as ion-exchange materials, the survey covering the preparation, properties, uses and theory of these materials.

Le microdosage colorimétrique des phosphates dans des milieux divers (produits biologiques, pharmaceutiques et alimentaires): Gh. Ghimicescu and Vasile Dorneanu, *Talanta*, 1972, **19**, 263. (Institut de Médicine et de Pharmacie de Iassy, Roumanie.)

Summary—A colorimetric micromethod is proposed for determination of phosphates in various materials (biological substances, pharmaceuticals and food). It is based on precipitation of magnesium uranyl phosphate, which is then dissolved in dilute sulphuric acid, and the uranyl ion is determined spectrophotometrically *via* the dark red colour of uranyl ferrocyanide. The sensitivity is 0·01 mg of P, and the average error 1%. The method is very simple and applicable to many types of sample.

Determination of platinum group metals, gold and silver by the tin collection scheme: G. H. Faye and P. E. Moloughney, *Talanta*, 1972, **19**, 269. (Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canda.)

Summary—A comprehensive analytical scheme is presented for the determination of the six platinum-group metals, gold and silver. It is the result of the integration of separate procedures that have been described previously, in part, over the course of several years. The analytical scheme has been thoroughly tested in umpire and standards work on a wide variety of materials and, as a consequence, is of increasing interest to many laboratories. The precious metals are collected in molten tin when the sample is fused at 1200–1250° with a flux containing stannic oxide, sodium carbonate, silica, borax and flour. The resultant tin alloy is dissolved and the precious metals are isolated by ion-exchange, solvent extraction and/or distillation procedures. With the exception of the usual facilities required in the fusion step of fire assaying, standard equipment can be used in the wet-chemical operations for the isolation and determination of the individual precious metals.

ИСКУССТВЕННЫЕ НЕОРГАНИЧЕСКИЕ ИОНООБМЕНИКИ—I. ГИДРАТИРОВАННЫЕ ОКИСЛЫ И КИСЛЫЕ СОЛИ МНОГОВАЛЕНТНЫХ ЭЛЕМЕНТОВ:

V. Veselý и V. Pekárek, *Talanta*, 1972, **19**, 219. (Институт Ядерных Исследований, Чехословацкая Академия Наук, Ржеж у Праги, Уехословакия.)

Резюме—В статье дан исчерпывающий литературный обзор об исползовании гидратированных окислов и кислых солей многовалентных элементов в качестве ионообмеников. Обзор включает способы приготовления, свойства, назначение и теорию этих материалов.

КОЛОРИМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ МИКРОДОЗ ФОСФАТОВ В РАЗЛИЧНЫХ СРЕДАХ (БИОЛОГИЧЕСКИХ, ФАРМАЦЕВТИЧЕСКИХ И ПИЩЕВЫХ ПРОДУКТОВ):

Gh. Ghimicescu and Vasile Dorneanu, *Talanta*, 1972, **19**, 263.

Резюме—Предлагается колориметрический метод для определения микроскопических доз фосфатов в различных материалах (биологических веществах, фармацевтических препаратах и в пищевых продуктах). Он основан на осаждении фосфата уранил-магния, который затем растворяется в разведённой серной кислоте, а ион уранила определяется спектрофотометрическим методом через темно-красный цвет уранил ферроцианида. Чувствительность метода = 0,01 мг P, ошибка в среднем 1 %. Метод отличается простотой и может применяться для многих видов образцов.

ОПРЕДЕЛЕНИЕ МЕТАЛЛОВ ПЛАТИНОВОЙ ГРУППЫ, ЗОЛОТА И СЕРЕБРА МЕТОДОМ СБОРА В ОЛОВЕ:

G. H. Faye and P. E. Moloughney, *Talanta*, 1972, **19**, 269.

Резюме—Предлагается исчерпывающая аналитическая схема для определения 6-ти металлов платиновой группы, золота и серебра. Она получена в результате суммирования отдельных процедур, которые частично описывались в течение нескольких лет. Эта аналитическая схема тщательно проверена при специальной испытательной и стандартной работе с широким рядом материалов и, вследствие этого, интерес в ней для многих лабораторий возрастает. Благородные металлы собираются в расплавленном олове, причем образец расплавляется при 1200–1250° температуре флюсом, содержащем окись олова, углекислый натрий, двуокись кремния, буру и муку. Полученный сплав олова растворяется, а благородные металлы изолируются путем ионнообмена, экстрагирования растворителя и/или дистилляцией. За исключением обычных средств расплавления для определения сухим путем при высоких температурах, можно применять стандартное оборудование в мокрых химических операциях для отделения и определения отдельных благородных металлов.

Kinetic method of analysis by analogue computer simulation: Masaki Nakanishi, *Talanta*, 1972, **19**, 285. (Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo, Japan.)

Summary—The simulation by an analogue computer of slow reactions used for the purpose of chemical analysis is described. Bromination of maleic and fumaric acids is used for illustration. The concentration of bromine is traced spectrophotometrically as a function of time and the trace simulated with an analogue computer by the trial and error method. The initial concentration of the substance in question and the rate constant of the reaction are determined from the values given to the computer variables to obtain the best fit. Only a single experiment is required for the analysis. The procedure can be followed easily without laborious mathematical or graphical treatment.

Möglichkeiten und Grenzen bei der Verwendung von Filterpapier als Träger bei der röntgenspektrometrischen Analyse: G. Ackermann, R.-K. Koch, H. Ehrhardt und G. Sanner, *Talanta*, 1972, **19**, 293. (Bergakademie Freiberg, Sektion Chemie—Lehrstuhl für Analytische Chemie und VEB Bergbau und Hüttenkombinat "Albert Funk"—Forschungsinstitut für NE-Metalle, Freiberg (Sachs), DDR.)

Summary—It has been shown that filter paper is a suitable support material for X-ray fluorescence analysis, but that the use of the Weisz ring-oven enables a higher sensitivity to be obtained with a sufficiently reproducible sample geometry. Linear calibration plots are obtained for Ag, Pd, Rh, Pt, Au, Cu, Fe and Ca in the range 0–100 μg. The relative standard deviations vary between 7 and 35, and the limits of detection range from 8 to 35 μg/ml (for iron and calcium respectively). Five samples may be analysed in 30 min. Use of the wax-ring technique enables the analysis time to be halved, but the sensitivity is then less.

Electrophoretic determination of pK-values of indicators and their relation to colour changes: I. Mori, M. Shinogi, E. Falk and Y. Kiso, *Talanta*, 1972, **19**, 299. (Kobe Pharmaceutical Women's College, Nakano 450, Motoyama-cho, Higashi-Nada-Ku, Kobe, Japan and Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osakafu, Japan.)

Summary—The pK-values of Xylenol Orange, Pyrocatechol Violet, Thorin and Alizarin Complexone were determined electrophoretically on the basis of the Kiso equation. The colour changes of Xylenol Orange and Alizarin Complexone were found to take place at slightly higher pH values than the electrophoretically determined pK-values. The Kiso-equation for the determination of pK values by electrophoresis yielded reproducible results and the method is useful for complicated substances because the procedure is simple, the equipment inexpensive and only microamounts of the substances are needed.

КИНЕТИЧЕСКИЙ МЕТОД АНАЛИЗА АНАЛОГОВОЙ ВЫЧИСЛИТЕЛЬНОЙ МАШИНОЙ:

Masaki Nakanishi, *Talanta*, 1972, **19**, 285.

Резюме—Описывается воспроизведение медленных реакций при помощи аналоговой вычислительной машины в целях химических анализов. Для иллюстрирования проводилось бромирование малеиновой и фумаровой кислот Концентрация брома прослеживалась спектрофотометрически, как функция времени и моделировалась аналоговой вычислительной машиной методом проб и ошибок. Начальная концентрация данного вещества и константа скорости реакции определялись по величинам переменных, даваемых вычислительной машине, чтобы получать наиболее подходящее соответствие. Для анализа требуется только один эксперимент. Процедура проделывается легко, без трудоёмких математических или графических приемов.

ВОЗМОЖНОСТИ И ОГРАНИЧЕНИЯ ИСПОЛЬЗОВАНИЯ ФИЛЬТРОВАЛЬНОЙ БУМАГИ КАК НОСИТЕЛЯ ПРИ АНАЛИЗАХ РЕНТГЕНОВСКОЙ СПЕКТРОМЕТРИЕЙ:

G. Ackermann, R.-K. Koch, H. Ehrhardt and G. Sanner, *Talanta*, 1972, **19**, 293.

Резюме—Показано, что фильтровальная бумага является хорошим поддерживающим материалом для анализа рентгеновской флуоресценцией, но употребление кольцевой печи Вейша увеличивает получаемую чувствительность с достаточно воспроизводимой геометрией образца. Для Ag, Pd, Rh, Pt, Au, Cu, Fe и Ca получены линейные калибровочные графики в диапазоне 0–100 uг. Стандартные относительные отклонения колеблются между 7 и 35, а границы диапазона определения от 8 до 35 uг/мл (для железа и кальция соответственно). В течение 30-ти минут можно проанализировать 5 образцов. Применение техники воскового кольца укорачивает время анализа на половину, но тогда чувствительность уменьшается.

ОПРЕДЕЛЕНИЕ ЭЛЕКТРОФОРЕЗОМ ЗНАЧЕНИЙ pK ИНДИКАТОРОВ И И ИХ ОТНОШЕНИЕ К ИЗМЕНЕНИЮ ЦВЕТА:

I. Mori, M. Shinogi, E. Falk and Y. Kiso, *Talanta*, 1972, **19**, 299.

Резюме—Электрофорезом на основании уравнения Kiso были определены значения pK для красок: ксиленол-оранжевой, пирокатехин-фиолетовой, торин и ализарин комплексона. Изменения цвета ксиленол оранжевой и ализаринового комплексона имели место при более высоких значениях pH, чем определенные электрофорезом значения pK. Уравнение Kiso для определения значений pK электрофорезом дало воспроизводимые результаты; этот метод хорош для сложных веществ, так как процедура простая, оборудование недорогое и требуются только микроскопические количества веществ.

Application of displacement reactions in flame photometry–II. Emission flame photometric determination of alkaline earth metals in the presence of interfering anions: P. J. SLEVIN, E. GYÖRY-SZEBÉNYI and G. SVEHLA, *Talanta*, 1972, **19**, 307. (Department of Chemistry, Queen's University, Belfast, U.K.)

Summary—For the emission flame photometric determination of strontium and barium in the presence of interfering ions such as phosphate, sulphate, arsenate and oxalate, calibration or simple standard addition methods cannot be used. Greatly reduced errors can be achieved by dividing the sample solution into four equal parts and adding to each certain known amounts of two metal ions. One of these is identical to the determinand (*e.g.*, strontium or barium) the other has similar characteristics to it (*e.g.*, calcium). The amounts of these metals are chosen so that the total (molar) concentration of these should be identical in all solutions, but the ratio of the concentrations of the two metals should be different. The emission of the determinand metal must be measured, and a standard addition plot produced. The amount of determinand present in the sample can be obtained from the intersection of the emission *vs.* concentration line with the concentration axis.

A fully automated procedure for the determination of sodium hypochlorite and hydrogen peroxide, based on the use of a porous catalytic silver electrode: B. FLEET, A. Y. W. HO and J. TENYGL, *Talanta*, 1972, **19**, 317. (Department of Chemistry, Imperial College of Science and Technology, London, S.W.7, U.K. and Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Czechoslovakia.)

Summary—A new approach to the automated determination of sodium hypochlorite and hydrogen peroxide is described, based on the use of a porous catalytic silver electrode. The principle of both methods involves the quantitative liberation of oxygen, which is measured coulometrically by the electrode. The procedures are suitable for the continuous monitoring of the contents of bleaching baths.

ПРИМЕНЕНИЕ РЕАКЦИЙ СМЕЩЕНИЯ В ПЛАМЕННОЙ ФОТОМЕТРИИ—ОПРЕДЕЛЕНИЕ ЩЕЛОЧНЫХ ЗЕМЕЛЬНЫХ МЕТАЛЛОВ ПОСРЕДСТВОМ ПЛАМЕННОЙ ФОТОМЕТРИИ ЭМИССИИ II В ПРИСУТСТВИИ ИНТЕРФЕРИРУЮЩИХ АНИОНОВ:

P. J. Slevin, E. Györy-Szebényi and G. Svehla, *Talanta*, 1972, **19**, 307.

Резюме—Калибровочный или простой стандартный метод добавления не могут применяться для определения пламенной фотометрией эмиссии стронция и бария в присутствии интерфериующих ионов, как напр. фосфатов, сульфатов, арсенатов и оксалатов. Можно значительно уменьшить ошибки, разделяя раствор образца на 4 равные части и добавляя к каждой известное количество ионов двух металлов. Один из них должен быть идентичен с детермтнантом (т.е. стронцием или барием), второй должен иметь подобные ему характеристики (напр. кальций). Количества этих металлов выбираются таким образом, чтобы общая (молярная) концентрация их была одинакова во всех растворах, но чтобы соотношение концентраций двух металлов было различно. Затем измеряется эмиссия металла-детерминанта и составляется стандартный график добавления. Количество детерминанта в образце получается на пересечении эмиссии против линии концентрации с осью концентрации.

ПОЛНОСТЬЮ АВТОМАТИЗИРОВАННАЯ ПРОЦЕДУРА ДЛЯ ОПРЕДЕЛЕНИЯ ГИПОХЛОРИТА НАТРИЯ И ПЕРЕКИСИ ВОДОРОДА, ОСНОВАННАЯ НА ИСПОЛЬЗОВАНИИ ПОРИСТОГО СЕРЕБРЯНОГО, КАТАЛИТИЧЕСКОГО, ЭЛЕКТРОДА:

B. Fleet, A. Y. W. Ho and J. Tenygl, *Talanta*, 1972, **19**, 317.

Резюме—Описывается основанный на использовании пористого каталитического серебряного электрода новый подход для определения гипохлорита натрия и перекиси водорода. Принцип обоих методов основан на выделении количеств кислорода, которые измеряются электродом кулонометрически. Эти процедуры могут применяться для непрерывного регулирования содержимого отбеливающих ванн.

Study of oxidation state of plutonium in solution, by flow-coulometric method: SORIN KIHARA, TADASHI YAMAMOTO, KENJI MOTOJIMA and TAITIRO FUJINAGA, *Talanta*, 1972, **19**, 329. (Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan and Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto, Japan.)

Summary—Reduction rates of Pu(IV) and oxidation rates of Pu(III) have been studied in sulphuric acid and nitric acid media, as functions of acid concentration, plutonium concentration and kind of acid. A flow-coulometric method was used in this work. This procedure has many merits, namely, the sample size required is very small, special reagents are not used, fewer limitations are imposed by the type and concentration of acid, and the method is rapid.

Spectrophotometric determination of 0–50 ng of chromium in 1 ml of human serum: J. AGTERDENBOS, L. VAN BROEKHOVEN, B.A.H.G. JÜTTE and J. SCHURING, *Talanta*, 1972, **19**, 341. (Analytisch-Chemisch Laboratorium, Rijksuniversiteit, Croesestraat 77A, Utrecht, Holland.)

Summary—A method is described for the determination of chromium in 1 ml of human serum or plasma. It is based on a wet decomposition and a spectrophotometric determination with diphenylcarbazide after extraction with methyl isobutyl ketone. A 40-mm cuvette with less than 1 ml sample volume is described. Results are lower than expected from the literature, most samples from healthy persons containing less than 2 or 3 ng/ml. The reproducibility is about 1 ng/ml.

Dichloramine-T as a new oxidimetric titrant in non-aqueous and partially aqueous media: T. J. JACOB and C. G. R. NAIR, *Talanta*, 1972, **19**, 347. (University Department of Chemistry, Kerala University, Trivandrum-1, India.)

Summary—A new oxidimetric titrant, dichloramine-T, is proposed for redox titrations in glacial acetic acid medium. The general analytical conditions for using this oxidant and the procedures for potentiometric determination of ascorbic acid, iodide, arsenic(III) and iron(II) are described.

ИЗУЧЕНИЕ ОКИСЛЕНИЯ ПЛУТОНИЯ В РАСТВОРАХ ПРИ ПОМОЩИ СЧЕТЧИКА ПОТОКА (КУЛОНМЕТРА):

Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga, *Talanta*, 1972, **19**, 329.

Резюме—Изучались величины восстановления Pu(IV) и окисления Pu(III) в средах серной и азотной кислот, как функции концентрации и вида кислот и как функции концентрации плутония. Для этой работы пользовались кулометрическим методом. Эта процедура имеет много преимуществ, а именно: требуется очень небольшой образец, не требуется никаких специальных реактивов, вид и концентрация кислоты дают меньше ограничений и метод очень быстрый.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ 0–50 НГ ХРОМА В 1 МЛ. ЧЕЛОВЕЧЕСКОЙ СЫВОРОТКИ:

J. Agterdenbos, L. van Broekhoven, B. A. H. G. Jüffe and J. Schuring, *Talanta*, 1972, **19**, 341.

Резюме—Описывается метод определения хрома в 1 мл. человеческой сыворотки или плазмы. Он основан на влажном разложении и спектрофотометрическом определении с дифенилкарбазидом после экстрагирования метилизобутилкетоном. Описывается кюветка на 40 мм с образцом меньше 1 мл объемом. Результаты оказались ниже, чем описываемые в литературе; большая часть образцов от здоровых людей содержала меньше, чем 2 или 3 нг/мл. Воспроизводимость около 1 нг/мл.

ДИХЛОРАМИН-Т В КАЧЕСТВЕ НОВОГО ОКИСНОМЕТРИЧЕСКОГО ТИТРУЮЩЕГО АГЕНТА В БЕЗВОДНЫХ И ЧАСТИЧНО ВОДНЫХ СРЕДАХ:

T. J. Jacob and C. G. R. Nair, *Talanta*, 1972, **19**, 347.

Резюме—Для восетиновительно-окислительного титрования в среде ледяной уксусной кислоты предлагается новый окисномотрический титрующий агент—дихлорамин-Т. Описываются общие аналитические условия при использовании этого окислителя, а также процедуры для потенциометрического определения аскорбиновой кислоты, иода, машьяка (III) и железа (II).

Purity of compounds by extraction-solubility: R. A. HUMMEL and W. B. CRUMMETT, *Talanta*, 1972, **19**, 353. (Analytical Laboratories, 574 Building, The Dow Chemical Company, Midland, Michigan, U.S.A.)

Summary—Thirty-three organic compounds prepared for use as analytical standards were examined for purity by the extraction-solubility method. Of these, twenty-one gave satisfactory results, seven behaved non-ideally, and five were not soluble in the useful range. Results on the twenty-one satisfactory samples compared favourably with those obtained by differential scanning calorimetry and other analytical methods. The method was found to be useful for following the improvement of compounds undergoing purification.

Determination of phosphorus in lubricating oils by cool-flame emission spectroscopy: W. N. ELLIOTT, C. HEATHCOTE and R. A. MOSTYN, *Talanta*, 1972, **19**, 359. (Quality Assurance Directorate (Materials), Royal Arsenal, London, S.E.18.)

Summary—The phosphorus content of lubricating oils is determined by measurement of the emission from the HPO molecular species at 528 nm in a cool hydrogen–nitrogen diffusion flame. The oil is ashed in the presence of potassium hydroxide and an aqueous extract of the melt is treated with ion-exchange resin to remove interferents, before aspiration into the flame. Analytical results are presented on samples containing phosphorus in the range 0.009–0.2%. The precision of the method is ±5% at the 0.04% phosphorus level.

Neutron-activation analysis for thorium in zircon: H. B. DESAI, R. PARTHASARATHY and M. SANKAR DAS, *Talanta*, 1972, **19**, 363. (Analytical Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-85 (AS), India.)

Summary—The thorium content of zircons and standard rock samples was determined by neutron-activation analysis. The 310-keV photopeak activity of ^{233}Pa was enhanced by a prior chemical separation which removed interfering induced activities.

ПРОВЕРКА ЧИСТОТЫ СОЕДИНЕНИЙ МЕТОДОМ ЭКСТРАГИРОВАНИЯ/РАСТВОРИМОСТИ:

R. A. HUMMEL and W. B. CRUMMETT, *Talanta*, 1972, **19**, 353.

Резюме—Приготовленные для использования в качестве аналитических стандартов тридцать три органические соединения проверялись на чистоту методом экстрагирования—растворимости. Из них двадцать одно соединение дало удовлетворительные результаты, семь—не очень хорошие, а пять не растворялись в требуемых пределах. Результаты двадцати одного удовлетворительного образца имели преимущества по сравнению с методом дифференциальной развертывающей калориметрии и с другими аналитическими методами. Метод оказался полезным для проверки улучшения соединений, подвергаемых очистке.

ОПРЕДЕЛЕНИЕ ФОСФОРА В СМАЗОЧНЫХ МАСЛАХ СПЕКТРОСКОПИЕЙ С ЭМИССИЕЙ ХОЛОДНОГО ПЛАМЕНИ:

W. N. ELLIOTT, C. HEATHCOTE and R. A. MOSTYN, *Talanta*, 1972, **19**, 359.

Резюме—Содержание фосфора в смазочных маслах определялось измерением эмиссии от видов молекул HPO при 528 нм в холодном диффузионном пламени водород-азот. В присутствии гидроокиси калия масло превращалось в золу и перед отсосом в пламя водный экстракт расплава обрабатывался ионообменной смолой для удаления интерферирующих веществ. Аналитические результаты представлены на образцах, содержащих фосфор в пределах 0,009–0,2 %. Точность метода ± 5 % при уровне фосфора = 0,04 %.

АНАЛИЗ НЕЙТРОННОЙ АКТИВАЦИИ ДЛЯ ОПРЕДЕЛЕНИЯ ТОРИЯ В ЦИРКОНИИ:

H. B. DESAI, R. PARTHASARATHY and M. SANKAR DAS, *Talanta*, 1972, **19**, 363.

Резюме—Содержание тория в циркониевых и стандартных образцах горных пород определялось анализом нейтронной активации. Максимальная фотоактивность ^{233}Pa в 310 кэв усиливалась предварительным химическим отделением, которое устраняло интерферирующую искусственную радиоактивность.

Spectrophotometric molybdenum determination with thiolactic acid: JAMES S. FRITZ and DONALD R. BEUERMAN, *Talanta*, 1972, **19**, 366. (Iowa State University, Ames, Iowa, U.S.A.)

Summary—A quick, selective method for molybdenum(VI) is based on the formation of a yellow thiolactic acid complex. The complex is formed at pH 1.0–1.6, and the absorbance is measured at 365 nm.

Determination of traces of iron(II) in the presence of iron(III) by the bathophenanthroline method: TAKAYUKI MIZUNO, *Talanta*, 1972, **19**, 369. (Technical Laboratory, Central Research Institute of Electrical Power Industry, Iwato, Komae, Tokyo, Japan.)

Summary—Traces of iron(II) (1–30 ppM) in the presence of iron(III) were determined (error <10%) by the bathophenanthroline method. Interference of iron(III) was eliminated by masking with sodium pyrophosphate (2·5–60 mg). The iron(II) complex was extracted with n-butanol, at pH 4·2–4·7.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МОЛИБДЕНА ПОСРЕДСТВОМ ТИОМОЛОЧНОЙ КИСЛОТЫ:

JAMES S. FRITZ and DONALD R. BEUERMAN, *Talanta*, 1972, **19**, 366.

Резюме—Быстрый селективный метод для молибдена(VI), основанный на образовании желтого комплексного соединения тиомолочной кислоты. Соединение это образуется при pH = 1,0–1,6, поглощаемость измеряется при 365 nm.

ОПРЕДЕЛЕНИЕ СЛЕДОВ ЖЕЛЕЗА (II) В ПРИСУТСТВИИ ЖЕЛЕЗА (III) БАТОФЕНАНТРОЛИНОВЫМ МЕТОДОМ:

TAKAYUKI MIZUNO, *Talanta*, 1972, **19**, 369.

Резюме—Следы железа (II) (1–30 ч/милл в присутствии железа (III) определялись батофенантролиновым методом (ошибка $<10\%$). Интерференция железа(III) исключалась маскировкой пирофосфатом натрия (2,5–60 мг). Комплекс железа(II) извлекался н-бутанолом при pH = 4,2–4,7.

Determination of inorganic impurities in vinyl chloride by activation analysis: FLORIN T. BUNUŞ and SANDA MURGALESCU, *Talanta*, 1972, **19**, 372. (Institute of Atomic Physics, Bucharest, Romania.)

Summary—Trace impurities in vinyl chloride have been determined by activation analysis in a reactor thermal neutron flux of $1{\cdot}2 \times 10^9$ $n/mm^2/sec$. Irradiations were carried out on liquid and solid samples at the same time as a standard. Gamma-spectrometry was used to reveal the presence of arsenic and bromine, the quantitative estimation being based on two calculus methods. The impurities determined were: arsenic $8{\cdot}0 \pm 0{\cdot}6 \times 10^{-4}\%$, bromine $3{\cdot}07 \pm 0{\cdot}2 \times 10^{-3}\%$ and phosphorus $2{\cdot}0 \pm 0{\cdot}15 \times 10^{-2}\%$.

Organic and inorganic ion-exchange beads as indicators in redox and precipitation titrations: MOHSIN QURESHI, SAIDUL ZAFAR QURESHI and NIGHAT ZEHRA, *Talanta*, 1972, **19**, 377. (Chemistry Department, Aligarh Muslim University, Aligarh (U.P.), India.)

Summary—Resin beads in the Fe(III) or *p*-dimethylaminobenzylidenerhodanine form are used as indicators in precipitation titrations with $K_3Fe(CN)_6$ and Ag^+. Resin beads with diphenylamine adsorbed on them can be used as indicators in cerimetric titrations. They have some advantages over conventional indicators.

On the analytical utility of quasi-linear molecular emission spectra: R. J. LUKASIEWICZ and J. D. WINEFORDNER, *Talanta*, 1972, **19**, 381. (Department of Chemistry, University of Florida, Gainesville, Florida 32601, U.S.A.)

Summary—The analytical utility of the Shpol'skii effect has been examined. It is concluded that the combined instrumental and theoretical restrictions limit the analytical usefulness of true quasi-line spectra for quantitative work.

ОПРЕДЕЛЕНИЕ НЕОРГАНИЧЕСКИХ ПРИМЕСЕЙ В ВИНИЛХЛОРИДЕ АКТИВАЦИОННЫМ АНАЛИЗОМ:

Florin T. Bunuş and Sandra Murgalescu, *Talanta*, 1972, **19**, 372.

Резюме—Следы примесей в винихлориде были определены активационным анализом в реакторе с тепловым нейтронным потоком в $1,2 \times 10^9$ н/мм^2/сек. Проводилось облучение жидкости и одновременно твердых образцов, как стандартов. Для обнаружения присутствия мышьяка и брома пользовались гамиа-спектрометрией, причем количественное определение основывалось на двух методах исчисления. Были определены следующие примеси: мышьяка $8,0 \pm 0,6 \times 10^{-4}\%$, брома $3,07 \pm 0,2 \times 10^{-4}\%$ и фосфора $2,0 \pm 0,15 \times 10^{-2}\%$.

ОРГАНИЧЕСКИЕ И НЕОРГАНИЧЕСКИЕ ИОНООБМЕННЫЕ ГРАНУЛЫ, КАК ИНДИКАТОРЫ ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНОГО И ОСАДИТЕЛЬНОГО ТИТРОВАНИЯ:

Mohsin Qureshi, Saidul Zafar Qureshi and Nighat Zehra, *Talanta*, 1972, **19**, 377.

Резюме—Гранулы смолы в виде Fe(III) или в форме р-диметиламинобензилиденеροданина применялись как индикаторы при титровании с $K_3Fe(CN)_6$ и Ag^+. Смоляные гранулы с адсорбированным на них дифениламином могут служить индикаторами для цериметрических титрований. Они имеют некоторые преимущества перед обычными индикаторами.

ОБ АНАЛИТИЧЕСКОМ ИСПОЛЬЗОВАНИИ КВАЗИЛИНЕЙНОГО МОЛЕКУЛЯРНОГО СПЕКТРА ЭМИССИИ:

R. J. Lukasiewicz and J. D. Winefordner, *Talanta*, 1972, **19**, 381.

Резюме—Проверялось аналитическое использование эффекта Shpol'ского. Заключение: сочетание приборных и теоретических пределов ограничивает аналитическое использование настоящего квазилинейного спектра для количественного определения.

SUMMARIES FOR CARD INDEXES

Synthetic inorganic ion exchangers—II. Salts of heteropolyacids, insoluble ferrocyanides, synthetic aluminosilicates and miscellaneous exchangers: V. Pekárek and V. Veselý, *Talanta*, 1972, **19**, 1245. (Nuclear Research Institute of the Czechoslovak Academy of Sciences, Řež near Prague, Czechoslovakia.)

Summary—A review of the developments during the period 1965–70 in use of heteropoly acid salts, ferrocyanides and synthetic zeolites as ion-exchangers.

A contribution to the problem of increasing the sensitivity of anodic-stripping voltammetry: Ludmila Huderová and Karel Štulík, *Talanta*, 1972, **19**, 1285. (Research Institute for Pharmacy and Biochemistry, and Department of Analytical Chemistry, Charles University, Prague, Czechoslovakia.)

Summary—A brief discussion of problems connected with increasing the sensitivity of anodic-stripping determinations is presented. A new microcell for anodic-stripping voltammetry in solution volumes down to about 0.01 ml was constructed. The effect of the solution volume, the mercury-drop electrode size, and of the pre-electrolysis time and potential on the sensitivity of determinations was studied and the reproducibility of results for determinations of lead in mineral acids is given. It was found that nanogram amounts of heavy metals can easily be determined in this way. In determination of 2 ng of Pb^{2+} in 0.02 ml of solution the results were 2.00 ± 0.13 ng (95% confidence limits), the mean relative deviation being 6.3%. For determination of copper in KNO_3, stripping microanalysis was compared with atomic-absorption spectrophotometry. Advantages and disadvantages of stripping voltammetry on the macro- and micro-scales are discussed.

Determination of and differentiation between cassiterite and silicate-bound tin in silicate rocks containing traces of tin: J. Agterdenbos and J. Vlogtman, *Talanta*, 1972, **19**, 1295. (Laboratory for Analytical Chemistry, State University, Croesestraat 77A, Utrecht, Holland.)

Summary—A simple, sensitive and reproducible method is described for the determination of tin in silicate rocks at the ppm level. By applying a selective decomposition it seems possible to differentiate between tin present in the silicate lattice, in readily-accessible cassiterite (SnO_2) and in cassiterite enclosed in the silicate. The final determination is made by extraction and photometry with phenylfluorone. Results for total tin agree well with those obtained by X-ray fluorescence.

СИНТЕТИЧЕСКИЕ НЕОРГАНИЧЕСКИЕ ИОНООБМЕННИКИ—II. СОЛИ ГЕТЕРОПОЛИКИСЛОТ, НЕРАСТВОРИМЫЕ ФЕРРОЦИАНИДЫ, СИНТЕТИЧЕСКИЕ АЛЮМОСИЛИКАТЫ И РАЗНЫЕ ОБМЕННИКИ:

V. Pekárek and V. Veselý, *Talanta*, 1972, **19**, 1245.

Резюме—Приведен обзор успехов полученных в периоде 1965–70 при использовании гетерополикислот, ферроцианидов и синтетических зеолитов в качестве ионообменников.

ВКЛАД В ПРОБЛЕМУ ПОВЫШЕНИЯ ЧУВСТВИТЕЛЬНОСТИ МЕТОДА ВОЛЬТАМПЕРОМЕТРИИ С АНОДНЫМ СНИМАНИЕМ:

Ludmila Huderová and K. Štulík, *Talanta*, 1972, **19**, 1285.

Резюме—Кратко рассмотрены проблемы своязанные с повышением чувствительности вольтамперометрии с анодным сниманием. Сконструирована новая микроячейка лдя применения метода в растворах, использующая объемы вплоть до 0,01 мл. Изучено влияние объема раствора, размеров капельного ртутного электрода, продолжительности предварительного электролиза и потенциала на чувствительность определений и определена воспроизводимость результатов полученных в определении свинца в минеральных кислотах. Метод позволяет определять нанограммовые количества тяжёлых металлов. При определении 2 нг Pb^{2+} в 0,02 мл раствора получено 2,00 ± 0,13 нг (с пределем доверия 95 %), с относительной стандартной ошибкой 6,3 %. В случае определения меди в KNO_3 микроанализ обсужденным методом сравнен с методом атомно-абсорбционной спектрофотометрии. Обсуждены преимущества и недостатки вольтамперометрии с анодным сниманием на макро- и микромасштабе.

ОПРЕДЕЛЕНИЕ И РАЗЛИЧЕНИЕ МЕЖДУ КАССИТЕРИТОМ И СВЯЗАННЫМ С СИЛИКАТОМ ОЛОВОМ В СИЛИКАТНЫХ ГОРНЫХ ПОРОДАХ СОДЕРЖАЩИХ СЛЕДЫ ОЛОВА:

J. Agterdenbos and J. Vlogtman, *Talanta*, 1972, **19**, 1295.

Резюме—Описан несложный, чувствительный и воёпроизводимый метод определения олова в силикатных горных породах в области частей на миллион. Применение селективного разложения пробы позволяет различать между оловом присутствующим в силикатной решётке, в легкодоступном касситерите (SnO_2) и в касситерите, закрытом в силикате. Конечное определение состоит из экстрагирования и фотометрического определения с фенилфлуороном в качестве реагента. Результаты полученные для общего содержания олова хорошо соглашаются с результатами полученными методом рентгеновской флуоресценции.

Determination of manganese by atomic-fluorescence spectroscopy using a carbon-filament atom-reservoir: L. Ebdon, G. F. Kirkbright and T. S. West, *Talanta*, 1972, **19**, 1301. (Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AY, U.K.).

Summary—The atomic-fluorescence characteristics of manganese heated on a carbon-filament atom-reservoir (CFAR) are described and compared with (*a*) the atomic-absorption behaviour of the element on the same filament apparatus, and (*b*) its fluorescence behaviour in a separated air–acetylene flame. By fluorescence at 279·5 nm, using 1-μl samples, manganese may be determined down to 0·6 pg (6×10^{-4} ppm) by use of an electrodeless discharge lamp source (3 pg or 3×10^{-3} ppm by absorption, and 20 ng or 1×10^{-2} ppm by flame emission at 403 nm). The effects of fourteen representative cations and anions examined showed no interference at 10-fold and 100-fold levels and serious interference only from magnesium at the 1000-fold level, with *ca.* 10% suppression from Cr, V, Na and K. No fluorescence signals were observed at any wavelength other than 279·5 nm when the CFAR device was used.

Some considerations on spectral line profiles of microwave-excited electrodeless discharge lamps: D. O. Cooke, R. M. Dagnall and T. S. West, *Talanta*, 1972, **19**, 1309. (Department of Chemistry, Imperial College of Science and Technology, London, SW7.)

Summary—The problems of line broadening in microwave-excited electrodeless discharge lamps for the more volatile elements, P, S, I, Se, Zn, Cd and Hg are discussed in relation to their use in atomic-absorption and fluorescence spectrometry. Both theoretical and practical implications are considered

---

Controlled potential coulometry: the application of a secondary reaction to the determination of plutonium and uranium at a solid electrode: J. B. Fardon and I. R. McGowan, *Talanta*, 1972, **19**, 1321. (British Nuclear Fuels Ltd., Windscale and Calder Works, Sellafield, Seascale, Cumberland, U.K.)

Summary—A method is described for the simultaneous determination of plutonium and uranium in mixed oxides by controlled potential coulometry at a gold working electrode in two stages: first a coulometric oxidation, at 0·73 V *vs.* a silver/silver chloride electrode, of Pu(III) and U(IV) to Pu(IV) and U(VI) by a combination of a direct electrode reaction and a secondary chemical reaction proceeding concurrently, and secondly, a coulometric reduction at 0·33 V of Pu(IV) to Pu(III), leaving uranium as U(VI). The determination is carried out in a mixture of sulphuric and nitric acids, and Ti(III) is used to reduce plutonium and uranium to Pu(III) and U(IV) before electrolysis. The precision (3σ) of Pu:U ratio results obtained from mixtures containing about 30% and 2% plutonium was 0·5% and 1·5% respectively. The effect of experimental variables on the time taken to complete the coulometric determination is discussed.

ОПРЕДЕЛЕНИЕ МАРГАНЦА МЕТОДОМ АТОМНО-ФЛУОРЕСЦЕНТНОЙ СПЕКТРОСКОПИИ С ИСПОЛЬЗОВАНИЕМ АТОМНОГО РЕЗЕРВУАРА В ФОРМЕ УГОЛЬНОЙ НИТИ:

L. Ebdon, G. F. Kirkbright and T. S. West, *Talanta*, 1972, **19**, 1301.

Резюме—Описаны атомно-флуоресцентные характеристики марганца, нагреванного на атомном резервуаре в форме угольной нити (CFAR) и сравнены с (а) атомно-абсорбционными характеристиками элемента на том же приборе, и (б) его флуоресцентными характеристиками в отделенной пламены воздуха-ацетилена. Флуоресценция при 279,5 нм, с использованием 1 мкл пробы, позволяет определять марганец вплоть до 0,6 пг ($6 \cdot 10^{-4}$ ч. на миллион), применяя безэлектродную разрядную лампу (3 пг или $3 \cdot 10^{-3}$ ч. на миллион с применением абсорбции и 20 нг или $1 \cdot 10^{-2}$ ч. на миллион методом пламенной эмиссии при 403 нм). Испытанных 14 типических катионов и анионов не показали мешающее влияние при 10-кратном и 100-кратном избытке, а только магный показал серьезное влияние при 1000-кратном избытке; Cr, V, Na и K дали 10%-тное подавление сигнала. Никакие флуоресцентные сигналы не обнаружены при длинах волн других чем 279,5 нм при использовании прибора CFAR.

РАССМОТРЕНИЕ ПРОФИЛЕЙ ЛИНИЙ СПЕКТРА ВОЗБУЖДЕННЫХ МИКРОВОЛНАМИ БЕЗЭЛЕКТРОДНЫХ РАЗРЯДНЫХ ЛАМП:

D. O. Cooke, R. M. Dagnall and T. S. West, *Talanta*, 1972, **19**, 1309.

Резюме—Рассмотрены проблемы расширения линий возбужденных микроволнами безэлектродных разрядных ламп для более летучих элементов P, S, I, Se, Zn, Cd и Hg в связи с их использованием в атомно-абсорбционной и атомно-флуоресцентной спектроскопии. Проблема обсуждена с теоретической и практической точки зрения.

КУЛОНОМЕТРИЯ С РЕГУЛИРОВАННЫМ ПОТЕНЦИАЛОМ: ПРИМЕНЕНИЕ ВТОРИЧНОЙ РЕАКЦИИ В ОПРЕДЕЛЕНИИ ПЛУТОНИЯ И УРАНА НА ТВЁРДОМ ЭЛЕКТРОДЕ:

J. B. Fardon and I. R. McGowan, *Talanta*, 1972, **19**, 1321.

Резюме—Описан метод одновременного определения плутония

ОПРЕДЕЛЕНИЕ ПЛУТОНИЯ И УРАНА В СМЕШАННЫХ ОКСИДНЫХ ТОПЛИВАХ МЕТОДОМ ПОСЛЕДОВАТЕЛЬНОГО ОКИСЛИТЕЛЬНО-ВОССТАНОВИТЕЛЬНОГО ТИТРОВАНИЯ:

P. H. Chadwick and I. R. McGowan, *Talanta*, 1972, **19**, 1335.

Резюме—Последовательное определение урана и плутония в том же растворе пробы позволяет экономить с временем анализа и затратой для прибора. Метод начинает с U(IV) и Pu(III) в смеси серной и азотной кислот. Титрование дихроматом, применяя амперометрический метод на пары поляризируемых электродов, дает два хорошо выраженных конца титрования, соответствующие последовательному окислению U(IV) в U(VI) и Pu(III) в Pu(IV). Количественное окисление U(IV) в U(VI) получено путем действия Pu(IV) как промежуточного продукта, и зависит от создания условий способству-

Determination of trace metals in water by x-ray fluorescence spectrometry: H. Watanabe, S. Berman and D. S. Russell, *Talanta*, 1972, **19**, 1363. (Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada.)

Summary—A simple, rapid and accurate method for water analysis is proposed. The analytical procedure for the determination of Fe, Mn, Zn, Cu, Cd, As, Pb and Se in water in concentrations as low as a few ppM involves precipitation with a carrier of the metals by diethyldithiocarbamate (DDTC) or 1-(2-pyridylazo)-2-naphthol (PAN) and filtration through a Millipore filter. The precipitates collected on the filter disc are examined by X-ray fluorescence analysis. PAN is excellent for the determination of several metal ions at the ppM level, and DDTC can be used with tartrate as a masking agent if water samples contain large amounts of iron(III).

Studies on chromium(III) hydroxide, arsenate, antimonate, molybdate and tungstate: Mohsin Qureshi, Rajendra Kumar and H. S. Rathore, *Talanta*, 1972, **19**, 1377. (Chemical Laboratories, Aligarh Muslim University, Aligarh, U.P., India.)

Summary—Five water-insoluble compounds of chromium(III) have been synthesized by mixing 0·10*M* solutions of chromic chloride and the appropriate sodium salts in the volume ratio of 1:2, at pH 6–7. Their ion-exchange characteristics have been compared. The tungstate has the highest chemical stability and the arsenate has the highest ion-exchange capacity. Chromium(III) molybdate columns have been used to separate Pb^{2+} from numerous metal ions.

Investigations of dioximes and their metal complexes. A survey of the literature since 1963: Birgitta Egneus, *Talanta*, 1972, **19**, 1387. (Department of Analytical Chemistry, University of Gothenburg, Fack, S-402 20 Göteborg, Sweden.)

Summary—A review is given of the chemistry and analytical applications of dioxime complexes from metals.

ОПРЕДЕЛЕНИЕ СЛЕДОВ МЕТАЛЛОВ В ВОДЕ МЕТОДОМ РЕНТГЕНОВСКОЙ ФЛУОРЕСЦЕНЦИИ:

H. WATANABE, S. BERMAN and D. S. RUSSELL, *Talanta*, 1972, **19**, 1363.

Резюме—Предложен несложный, быстрый и прецизионный метод анализа воды. Методика определения Fe, Mn, Zn, Cu, Cd, As, Pb и Se в воде при концентрациях вплоть несколько частей на миллион основана на осаждении металлов в присутствии носителя диэтилдитиокарбаминатом (ДДТК) или 1-(2-пиридилазо)-2-нафтолом (ПАН), и фильтровании через Миллипор фильтр. Удержанные на фильтре осадки исследуют методом рентгеновской флуоресценции. ПАНом получены отличные результаты в определении ряда ионов металлов если присутствуют в микрограммовых количествах, а ДДТК может использоваться вместе с тартратом в качестве маскирующего агента в случае присутствия больших количеств железа(III) в пробе.

ИЗУЧЕНИЕ ГИДРООКИСИ, АРСЕНАТА, АНТИМОНАТА, МОЛИБДАТА И ВОЛЬФРАМАТА ХРОМА(III):

MOHSIN QURESHI, RAJENDRA KUMAR and H. S. RATHORE, *Talanta*, 1972, **19**, 1377.

Резюме—Приготовлено пять нерастворимых в воде соединений хрома(III) смешиванием 0,10*M* растворов хлорида хрома(III) и соответственных солей натрия, в объемном отношении 1:2, при pH 6–7. Сравнены их ионообменные характеристики. Вольфрамат обладает самой лучшой химической устойчивостью, а арсенат—самой лучшой ионообменной емкостью. Колонки молибдата хрома(III) использованы для отделения Pb^{2+} от многочисленных ионов металлов.

ИССЛЕДОВАНИЕ ДИОКСИМОВ И ИХ КОМПЛЕКСОВ С МЕТАЛЛАМИ. ОБЗОР ЛИТЕРАТУРЫ С 1963 ГОДА:

BIRGITTA EGNEUS, *Talanta*, 1972, **19**, 1387.

Резюме—Приведен обзор химии и применений в анализе комплексов диоксимов с металлами.

New masking procedure for selective complexometric determination of copper(II): Rajinder Pal Singh, *Talanta*, 1792, **19**, 1421. (Department of Chemistry, Panjabi University, Patiala, India.)

Summary—A study has been made of a new masking procedure for highly selective complexometric determination of copper(II), based on decomposition of the copper–EDTA complex at pH 5–6. Among the various combinations of masking agents tried, ternary masking mixtures comprising a main complexing agent (thiourea), a reducing agent (ascorbic acid) and an auxiliary complexing agent (thiosemicarbazide or a small amount of 1,10-phenanthroline or 2,2′-dipyridyl) have been found most suitable. An excess of EDTA is added and the surplus EDTA is back-titrated with lead (or zinc) nitrate with Xylenol Orange as indicator (pH 5–6). A masking mixture is then added to decompose the copper–EDTA complex and the liberated EDTA is again back-titrated with lead (or zinc) nitrate. The following cations do not interfere: Ag^+, Hg^{2+}, Pb^{2+}, Ni^{2+}, Bi^{3+}, As^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+}, Cd^{2+}, Co^{2+}, Cr^{3+} and moderate amounts of Fe^{3+} and Mn^{2+}. The notable feature is that consecutive determination of Hg^{2+} and Cu^{2+} can be conveniently carried out in the presence of other cations.

Volumetric determination of primary arylamines and nitrites, using an internal indicator system: Eugen Szekely, Amalia Bandel and Miriam Flitman, *Talanta*, 1972, **19**, 1429. (Department of Analytical Chemistry, Negev Institute for Arid Zone Research, Beer Sheva, Israel.)

Summary—A new nitrite titration method is presented. The titration is performed in the presence of a standard solution of 4,4′-sulphonyldianiline and diphenylamine, which is used as an internal indicator. An intense red colour develops during the titration as a result of a simultaneous diazotization and coupling process. A very sharp end-point is given by a colour change to yellow. The titration is performed at a temperature of about 45° in the presence of large amounts of nitrate. The method is specific and precise. It is suitable for the direct volumetric determination of various easily diazotized primary arylamines, sulphonamides and other amino-compounds which can be determined by nitrite titration. It is suitable also for the indirect determination of nitrites. The method is applicable on the semimicro and macro scales.

НОВЫЙ МЕТОД МАСКИРОВАНИЯ ДЛЯ СЕЛЕКТИВНОГО КОМПЛЕКСОНОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ МЕДИ(II):

RAJINDER PAL SINGH, *Talanta*, 1972, **19**, 1421.

Резюме—Изучен новый метод маскирования для высокоизбирательного комплексонометрического определения меди(II), основанного на разложении комплекса меди с ЭДТА при pH 5–6. Среди испытанных комбинаций маскирующих агентов найлучшие результаты получены тройними маскирующими смесями, состоящимися из главного комплексообразующего агента (тиомочевины), восстанавливающего агента (аскорбиновой кислоты) и вспомогательного комплексообразующего агента (тиосемикарбазида или небольщего количества 1,10-фенантролина или 2,2′-дипиридила). Раствору добавляют избыток ЭДТА который оттитруют раствором нитрата свинца (или цинка), с использованием ксиленолового оранжевого в качестве индикатора (pH 5–6). Раствору затем добавляют маскирующую смесь для разложения комплекса меди с ЭДТА, а выделенный ЭДТА снова оттитруют нитратом свинца (или цинка). Следующие катионы не мешают определению: Ag^+, Hg^{2+}, Pb^{2+}, Ni^{2+}, Bi^{3+}, As^{3+}, Al^{3+}, Sb^{3+}, Sn^{4+}, Cd^{2+}, Co^{2+}, Cr^{3+}, и умеренные количества Fe^{3+} и Mn^{2+}. Значительное преимущество метода в том, что им можно последовательно определять Hg^{2+} и Cu^{2+} в присутствии других катионов.

ОБЪЕМНОЕ ОПРЕДЕЛЕНИЕ ПЕРВИЧНЫХ АРИЛАМИНОВ И НИТРИТОВ С ИСПОЛЬЗОВАНИЕМ ВНУТРЕННОЙ ИНДИКАТОРНОЙ СИСТЕМЫ:

EUGEN SZEKELY, AMALIA BANDEL and MIRIAM FLITMAN, *Talanta*, 1972, **19**, 1429.

Резюме—Предложен новый метод титрования нитритов. Титрование проводится в присутствии титрованного раствора 4,4′-сульфонилдианилина и дифениламина, который служит в качестве внутренного индикатора. В течении титрования проявляется яркая красная окраска в результате одновременного протекания процессов диазотирования и сочетания. Весма острый конец титрования обнаруживается при переходе окраски в желтую. Титрование проводится при температуре около 45° в присутствии больших количеств нитрата. Метод является специфическим и прецизионным; им можно пользоваться для непосредственного объемного определения разных легко диазотированных первичных ариламинов, сульфонамидов и других аминосоединений, которые могут быть определены нитритным титрованием. Метод также применимый для косвенного определения нитритов, и может быть использован на семимикро- и макрошкале.

Arsenazo III and its analogues—VII. Coloured reactions of the rare earth elements with a new reagent—Carboxynitrazo: S. B. Savvin, T. V. Petrova and P. N. Romanov, *Talanta*, 1972, **19**, 1437. (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow.)

Summary—A new reagent, Carboxynitrazo, gives a colour reaction with some rare earth elements. For the individual rare earth elements the sensitivities of the reactions are very different. The difference is greatest for the elements of the Ce- and Y-subgroups. For the first subgroup the molar absorptivities are about 16×10^4 l. mole^{-1} cm^{-1}, whereas most of the elements of the Y-group do not give any colour reaction. A possible procedure for the determination of lanthanum in the presence of ytterbium is discussed.

Application of photon-counting in atomic-absorption spectrophotometry: R. M. Dagnall, B. L. Sharp and T. S. West, *Talanta*, 1972, **19**, 1442 (Chemistry Department, Imperial College of Science and Technology, London S.W.7.)

Summary—An analysis is given of the statistics of photon-counting as a means of making measurements in atomic-absorption spectrometry. It is concluded that the simple application of Poisson counting statistics may give an over-optimistic estimate of the error, since other sources of error, such as flame flicker and variable nebulization rate, may be more significant.

Some new applications of ferroin as redox indicator in titrations with dichromate: K. Sriramam, *Talanta*, 1972, **19**, 1445. (Department of Chemistry, Andhra University Postgraduate Centre, Guntur-5, Andhra Pradesh, India.)

Summary—Working conditions for the titration of arsenic(III), hydroquinone, ferrocyanide, uranium(IV) and molybdenum(V) with dichromate in sulphuric acid and hydrochloric acid media have been established, with ferroin as the redox indicator.

A note on successive complexometric determination of thorium and rare earths: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1972, **19**, 1448. (Analytical Laboratory, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—An improved method for successive determination of thorium and rare earths is described. It is based on the EDTA titration of thorium at pH 2 (Xylenol Orange as indicator) followed by addition of acetylacetone–acetone mixture, adjustment of the pH to 5–5·5 with hexamine, and by further EDTA titration of rare earths with the same indicator.

АРСЕНАЗО III И ЕГО АНАЛОГИ—VII: ЦВЕТНЫЕ РЕАКЦИИ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С НОВЫМ РЕАГЕНТОМ—КАРБОКСИНИТРАЗО:

S. B. SAVVIN, T. V. PETROVA and P. N. ROMANOV, *Talanta*, 1972, **19**, 1437.

Резюме—Новый реагент—карбоксинитразо—дает цветную реакцию с некоторыми редкоземельными элементами. Чувствительность реакций индивидуальных редкоземельных элементов весьма различается. Самая большая разница наблюдается для элементов подгрупп Се и У. В случае первой подгруппы молярные поглощения в порядке 16×10^4 л. моль. см$^{-1}$; большинство элементов группы У не дают цветной реакции. Обсуждена предложенная процедура для определения лантана в присутствии иттербия.

ПРИМЕНЕНИЕ СЧИТАНИЯ ФОТОНОВ В АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ:

R. M. DAGNALL, B. L. SHARP and T. S. WEST, *Talanta*, 1972, **19**, 1442.

Резюме—Приведен анализ статистики считания фотонов с целью применения в атомно-абсорбционной спектрофотометрии. Сделан вывод что простое применение статистики считания Пуассона может дать оптимистическую оценку ошибки, потому что другие источники ошибок, как на пример мерцание пламени и вариации в скорости распыления могут оказаться более значительными.

ТИТРОВАНИЕ МЫШЬЯКА(III) ХРОМОМ(VI) С ВИЗУАЛЬНЫМ ОБНАРУЖЕНИЕМ КОНЦА ТИТРОВАНИЯ:

K. SRIRAMAM, *Talanta*, 1972, **19**, 1445.

Резюме—Разработана методика для прямого и обратного титрования мышьяка(III) хромом(VI) до визуального конца титрования с использованием ферроина в качестве индикатора. Метод пользуется каталитическим эффектом однохлористого иода и железа(III) на индикаторные реакции в условиях титрования.

ПРИМЕЧАНИЯ К ПОСЛЕДОВАТЕЛЬНОМ ОПРЕДЕЛЕНИИ ТОРИЯ И РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ КОМПЛЕКСОНОМЕТРИЧЕСКИМ МЕТОДОМ:

RUDOLF PŘIBIL and VLADIMIR VESELÝ, *Talanta* 1972, **19**, 1448.

Резюме—Описан улучшенный метод последовательного определения тория и редкоземельных элементов. Метод основан на титровании тория с ЭДТА при pH 2 (с использованием ксиленолоранжевого в качестве индикатора), добавлении смеси ацетилацетона и ацетона, и дальнейшем титровании редкоземельных элементов с ЭДТА с использованием того же индикатора.

Spectrophotometric study of the reaction of bismuth(III) with Xylenol Orange: DONKA KANTCHEVA, PETRANA NENOVA and BORISLAV KARADAKOV, *Talanta*, 1972, **19**, 1450. (Department of Analytical Chemistry, Higher Institute of Chemical Technology and Metallurgy, Sofia-56, Bulgaria.)

Summary—The reaction between bismuth(III) and Xylenol Orange (XO) has been investigated by spectrophotometry. It has been established that bismuth(III) and Xylenol Orange form complex compounds with compositions Bi(III):XO = 1:1 (up to pH 1) and Bi(III):XO = 1:2 (above pH 1) which have absorption maxima at 550 and 500 nm respectively. The formula of the 1:1 complex is $[Bi(H_3R)]$ whereas the 1:2 complex can take one of the following forms: $[Bi(H_4R)_2]^{1-}$, $[Bi(H_4R)(H_3R)]^{2-}$ and $[Bi(H_3R)_2]^{3-}$.
If

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} \quad \text{and} \quad K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}}$$

the values for $pK_{Bi(H_3R)}$ and $pK_{Bi(H_3R)_2}$ respectively are 9·80 ± 0·03 and 15·53 ± 0·03 at a constant ionic strength of 1·0.

Radiochemical separation of zirconium and hafnium from other radionuclides, RICHARD B. HAHN, *Talanta*, 1972, **19**, 1454. (Analytical Sciences Division, U.K. Atomic Energy Research Establishment, Harwell, Berks., U.K.)

Summary—Radiozirconium and radiohafnium may be separated from all other radionuclides except scandium and protactinium by precipitation with mandelic acid from 5–10*M* hydrochloric acid, using commercial zirconyl chloride as carrier. Scandium and protactinium are removed by dissolving the precipitate in sodium carbonate, then adding barium nitrate to precipitate barium carbonate which acts as a scavenger. Zirconium mandelate is finally reprecipitated and the sample weighed and counted in this form. The method was checked by analysing commercial zirconyl chloride and standard rock samples for zirconium and hafnium by neutron-activation analysis.

Determination of phosphorus in phosphazenes and phosphines: SANFORD L. ERICKSON, *Talanta*, 1972, **19**, 1457. (Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.)

Summary—An improved technique for the determination of phosphorus in organic phosphazenes and phosphines is described. An acid digestion using a mixture of fuming nitric, sulphuric and perchloric acids converts the organically bound phosphorus into orthophosphate. The orthophosphate is precipitated as magnesium ammonium phosphate, which is ignited to magnesium pyrophosphate. With this technique phosphorus was determined in several compounds. The results establish both good accuracy and precision for the method.

ИЗУЧЕНИЕ СПЕКТРОФОТОМЕТРИЧЕСКИМ МЕТОДОМ РЕАКЦИИ ВИСМУТА(III) С КСИЛЕНОЛОВЫМ ОРАНЖЕВЫМ:

DONKA KANTCHEVA and B. KARADEKOV, *Talanta*, 1972, **19**, 1450.

Резюме—Изучена спектрофотометрическим методом реакция висмута(III) и ксиленолового оранжевого (КО). Установлено что висмут(III) и ксиленоловый оранжевый образуют комплексы состава Bi(III):КО = 1:1 (вплоть pH 1) и Bi(III):КО = 1:2 (выше pH 1), имеющие максимумы светопоглощения при 550 и 500 нм, соответственно. Формула комплекса 1:1 $[Bi(H_3R)]$, а комплекс 1:2 может имет одну из следующих форм: $[Bi(H_4R)_2]$, $[Bi(H_4R)(H_3R)]^{2-}$ и $[Bi(H_3R)_2]^{3-}$.
Если

$$K_{Bi(H_3R)} = \frac{[Bi^{3+}][H_3R^{3-}]}{[Bi(H_3R)]} \quad и \quad K_{Bi(H_3R)_2} = \frac{[Bi^{3+}][H_3R^{3-}]^2}{[Bi(H_3R)_2]^{3-}}$$

величины $pK_{Bi(H_3R)}$ и $pK_{Bi(H_3R)_2}$ равны 9,80 ± 0,03 и 15,53 ± 0,03, соответственно, при константной ионной силы 1,0.

РАДИОХИМИЧЕСКОЕ ОТДЕЛЕНИЕ ЦИРКОНИЯ И ГАФНИЯ ОТ ДРУГИХ РАДИОНУКЛИДОВ:

R. B. HAHN, *Talanta*, 1972, **19**, 1454.

Резюме—Радиоцирконий и радиогафний могуть быть отделены от всех других радионуклидов за исключением скандия и протактиния осаждением миндальной кислотой из раствора 5–10*M соляной кислоты*, с использованием коммерческого хлористого цирконила в качестве носителя. Скандий и протактиний устраняют растворением осадка в карбонате натрия и добавлением нитрата бария для осаждения карбоната бария который действует как собиратель. Затем переосаждают манделат циркония а пробу взвешивают и считают в этой форме. Метод испытан анализом коммерческого хлористого цирконила и стандартных образцев горных пород на цирконий и гафний методом нейтроноактивационного анализа.

ОПРЕДЕЛЕНИЕ ФОСФОРА В ФОСФАЗЕНАХ И ФОСФИНАХ:

SANFORD L. ERICKSON, *Talanta*, 1972, **19**, 1457.

Резюме—Описан улучшенный метод определения фосфора в органических фосфазенах и фосфинах. Фосфор в органической связи превращается в ортофосфат дигерированием с смесью дымящих азотной, серной и хлорной кислот. Ортофосфат затем осаждают в форме смешанного фосфата магния и аммония и сжигают до пирофосфата магния. Пользуясь этим методом фосфор определен в ряде соединений. Результаты показывают хорошую точность и воспроизводимость метода.

New tests for the detection of azide: G. S. JOHAR, *Talanta*, 1972, **19**, 1461. (Department of Chemistry, V.S.S.D. College, Kanpur-2, India.)

Summary—Two new, simple, reliable, and specific colour tests are described for the detection of azide. In one, the azide is heated with allyl isothiocyanate and water to form 1-allyl-2-tetrazoline-5-thione in solution; the latter gives a yellow precipitate on treatment with bismuth nitrate solution. Pyridine enhances the intensity of the colour. The allyl isothiocyanate can be produced *in situ* by treating allylamine with carbon disulphide, diethylamine and hydrogen peroxide. In the other test the azide is heated with carbon disulphide, water and acetone, resulting in the formation of 1,2,3,4-thiatriazoline-5-thione which gives a yellow precipitate with Cu(II) or Bi(III). Pyridine again enhances the colour. The method is applicable to 5–10 mg of soluble azides, but insoluble azides cannot be tested. CN^-, SCN^-, and other common anions do not interfere. Only S^{2-} interferes by masking the colour (black CuS or Bi_2S_3 is precipitated). NO_2^- in larger amounts interferes in the second test.

Potentiometric titration of heterocyclic nitrogen bases in non-aqueous media: K. C. MOHAN RAO and P. R. NAIDU, *Talanta*, 1972, **19**, 1465. (Physico-chemical Laboratories, Sri Venkateswara University, Tirupati (A.P.), India).

Summary—Pyridine, quinoline, isoquinoline, acridine, α-picoline, β-picoline, γ-picoline and 2,6-lutidine have been titrated potentiometrically (calomel and glass electrodes), with chlorosulphonic acid in methyl ethyl ketone–acetic acid (1:1) medium, with an error of less than 1%.

Rapid determination of selenium and tellurium by atomic-absorption spectrophotometry; B. C. SEVERNE and R. R. BROOKS, *Talanta*, 1972, **19**, 1467. (Department of Chemistry, Biochemistry, Biophysics, Massey University, Palmerston North, New Zealand.)

Summary—A rapid method has been developed for the determination of selenium and tellurium in geological and biological samples. It involves acid digestion of the sample with mineral acids, addition of arsenic as a carrier, reduction of arsenic to co-precipate selenium and tellurium, dissolution of the precipitate in dilute nitric acid and subsequent determination of selenium and tellurium by conventional atomic-absorption spectrophotometry. Selenium and tellurium have been measured on a routine basis, down to 0.1 ppm.

НОВЫЕ ПРОБЫ ДЛЯ ОТКРЫТИЯ АЗИДА:

G. S. Johar, *Talanta*, 1972, **19**, 1461.

Резюме—Описаны две новых, несложных, надёжных и специфических реакции для открытия азида. Для первой реакции азид нагревают с аллилизотиоцианатом и водой для образования 1-аллил-2-тетразолин-5-тиона в растворе. Это соединение дает желтый осадок с раствором нитрата висмута. Пиридин повышает интенсивность окраски. Аллилизотиоцианат может образоваться *in situ* обработкой аллиламина сероуглеродом, диэтиламином и перекисью водорода. В другой реакции азид нагревают с сероуглеродом, водой и ацетоном для образования 1,2,3,4-тиатриазолин-5-тиона, который дает желтый осадок с Cu(II) или Bi(III). Пиридин также повышает интенсивность окраски. Метод применим для 5–10 мг растворимых азидов, но методом не можно пользоватся в случае нерастворимых азидов. CN^-, SCN^- и другие обыкновенные анионы не мешают определению. Только S^{2-} маскирует цвет из-за осаждения черного CuS или Bi_2S_3. NO^{2-} в больших концентрациях мешает другой реакции.

ПОТЕНЦИОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ ГЕТЕРОЦИКЛИЧЕСКИХ ОРГАНИЧЕСКИХ ОСНОВАНИЙ В НЕВОДНЫХ СРЕДАХ:

K. C. Mohan-Rao and P. R. Naidu, *Talanta*, 1972, **19**, 1465.

Резюме—Проведены потенциометрические титрации пиридина, хинолина, изохинолина, акридина, α-пиколина, β-пиколина, γ-пиколина и 2,6-лутидина (пользуясь каломелевым и стеклянным электродами) с хлорсульфоновой кислотой в растворе метилэтилкетона и уксусной кислоты (1:1), с ошибкой меньше чем 1%.

БЫСТРОЕ ОПРЕДЕЛЕНИЕ СЕЛЕНА И ТЕЛЛУРА МЕТОДОМ АТОМНОАБСОРБЦИОННОЙ СПЕКТРОФОТОМЕТРИИ:

B. C. Severne and R. R. Brooks, *Talanta*, 1972, **19**, 1467.

Резюме—Разработан быстрый метод определения селена и теллура в геологических и биологических образцах. Метод основан на дигерировании образца минеральными кислотами, добавлении мышьяка в качестве носителя, восстановлении мышьяка для соосаждения селена и теллура, растворении осадка в разбавленной азотной кислоте и последующем определении селена и теллура методом атомноабсорбционной спектрофотометрии. Этим образом определяли концентрации селена и теллура вплоть 0,1 частей на миллион, пользующися методом для рутинного анализа.

Developments in indicators: L. Légrádi, *Talanta*, 1972, **19**, 1470. (Nitrokémia Works, Füzfögyártelep, Hungary.)

Summary—The use of metal ion–metallochromic indicator complexes as narrow-range pH indicators is shown to be advantageous for the titration of weak acids in aqueous media. The Cu–DBAH and the Mg–Azo Violet complexes with apparent p*K* values of 7·7 and 11·5 have been used for the titrations of benzoic acid and of glycine and phenol, respectively, with good precision.

Nouvelle microcolorimétrie des nitrities: Camelia Ghimicescu and Vasile Dorneanu, *Talanta*, 1972, **19**, 1474. (Laboratoire de Chimie Analytique de la Faculté de Pharmacie de Iassy, Roumanie.)

Summary—A micromethod for determination of nitrite is based on a reaction with *o*-tolidine, forming a yellow-orange product suitable for spectrophotometry. The sensitivity is 0·05 μg of nitrite/ml. The method is suitable for analysis of potable and mineral waters, and has a mean relative error of 1%.

Analytical application of the urease method for determination of urea in the presence of biuret: P. Bozadziev, E. Balabanova and L. Ilcheva, *Talanta*, 1972, **19**, 1477. (Chemico-Technological Institute, Sofia 56, Bulgaria.)

Summary—Biuret does *not* interfere in the urease-catalysed hydrolysis of urea.

Determination of gallium in an iron–aluminium matrix by solvent extraction and flame emission spectroscopy: M. S. Cresser and J. Torrent-Castellet, *Talanta*, 1972, **19**, 1478. (Department of Soil Science, University of Aberdeen, Scotland.)

Summary—Solvent extraction of gallium(III) into methyl isobutyl ketone from hydrochloric acid solutions containing titanium(III) sulphate provides a rapid method for separation of gallium from an iron/aluminium matrix and may be employed to eliminate the interference of these elements in the flame emission spectrometric determination of gallium.

Complexes of some rare earth metals with 1-amino-4-hydroxyanthraquinone: A. K. Jain†, V. P. Aggarwala, Puran Chand and S. P. Garg, *Talanta*, 1972, **19**, 1481. (Chemical Laboratories, University of Jodhpur, Jodhpur, India).

Summary—La, Ce(III), Pr, Nd and Sm(III) form very stable reddish-violet 1:1 complexes with 1-amino-4-hydroxyanthraquinone in methanol. The stability constants are very similar.

УСПЕХИ В ОБЛАСТИ ИНДИКАТОРОВ:

L. Légrádi, *Talanta*, 1972, **19**, 1470.

Резюме—Показано что использование комплексов ионов металлов с металлохромными индикаторами в качестве индикаторов для узких областей pH имеет известные преимущества в титровании слабых кислот в водных средах. Комплексы Cu-DBAH и Mg-азофиолетовый, имеющие кажущиеся величины pK 7,7 и 11,5, соответственно, успешно использованы в титровании бензойной кислоты, глицина и фенола.

НОВЫЙ МИКРОКОЛОРИМЕТРИЧЕСКИЙ МЕТОД ОПРЕДЕЛЕНИЯ НИТРИТОВ:

Camelia Ghimicescu and Vasile Dorneanu, *Talanta*, 1972, **19**, 1474.

Резюме—Микрометод определения нитрита основан на реакции с *о*-толидином, при которой образуется желто-оранжевая окраска, прикладная для спектрофотометрии. Чувствительность определения составляет 0,05 мкг нитрита/мл. Метод применимый в анализе питьевой и минеральных вод, а средная относительная ошибка метода составляет 1 %.

ПРИМЕНЕНИЕ МЕТОДА ДЛЯ ОПРЕДЕЛЕНИЯ МОЧЕВИНЫ С ПОМОЩЬЮ УРЕАЗЫ В ПРИСУТСТВИИ БИУРЕТА:

P. Bozadziev, E. Balabanova and L. Ilcheva, *Talanta*, 1972, **19**, 1477.

Резюме—Биурет не влияет на катализированный уреазой гидролиз мочевины.

ОПРЕДЕЛЕНИЕ ГАЛЛИЯ В МАТРИЦЕ ЖЕЛЕЗА-АЛЮМИНИЯ ЭКСТРАКЦИЕЙ РАСТВОРИТЕЛЕМ И МЕТОДОМ ПЛАМЕННОЙ СПЕКТРОСКОПИИ:

M. S. Cresser and J. Torrent-Castellet, *Talanta*, 1972, **19**, 1478.

Резюме—Экстракция галлия(III) метилизобутилкетоном из растворов соляной кислоты, содержащих сульфат титана(III), представляет собой быстрый метод выделения галлия из матрици железа-алюминия, которым можно пользоваться для устранения мешающего действия этих элементов в определении галлия методом пламенной спектроскопии.

КОМПЛЕКСЫ НЕКОТОРЫХ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ С 1-АМИНО-4-ОКСИАНТРАХИНОНОМ:

A. K. Jain, V. P. Aggarwala, Puran Chand and S. P. Garg, *Talanta*, 1972, **19**, 1481.

Резюме—La, Ce(III), Pr, Nd и Sm(III) образуют очень устойчивые комплексы 1:1 краснофиолетового цвета с 1-амино-4-оксиантрахиноном в метаноле. Константы устойчивости похожи.

A study of the evaporation of gold solutions: D. BUKSAK and A. CHOW, *Talanta*, 1972, **19**, 1483. (Department of Chemistry, University of Manitoba, Winnipeg, Canada.)

Summary—The study indicates that despite several reports to the contrary, gold does not volatilize appreciably during the evaporation of aqueous solutions. Gold solutions were shown to have a tendency to creep significantly in solutions of various metal concentrations, acid content and salt content, and that careful washing must be carried out to obtain quantitative recovery.

Modifications of the computer programme SCOGS: W. A. E. MCBRYDE and J. L. MCCOURT, *Talanta*, 1972, **19**, 1486. (Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.)

Summary—The computer programme SCOGS has been modified to accept and yield all equilibrium constants involving proton transfer, as concentration quotients. Significant savings in operating time are achieved through use of the FORTRAN H compiler.

ИЗУЧЕНИЕ ВЫПАРИВАНИЯ РАСТВОРОВ ЗОЛОТА:

D. Buksak and A. Chow, *Talanta*, 1972, **19**, 1483.

Резюме—Результаты изучения показывают что, несмотря на некоторые противоречащие отчеты, золото улетучивается только в незначительной мере при выпаривании водных растворов. Указано что растворы золота показывают значительную тенденцию ползучести в растворах содержащих различные концентрации других металлов, кислот и солей. Надо провести тщательную промивку для получения количественных выходов.

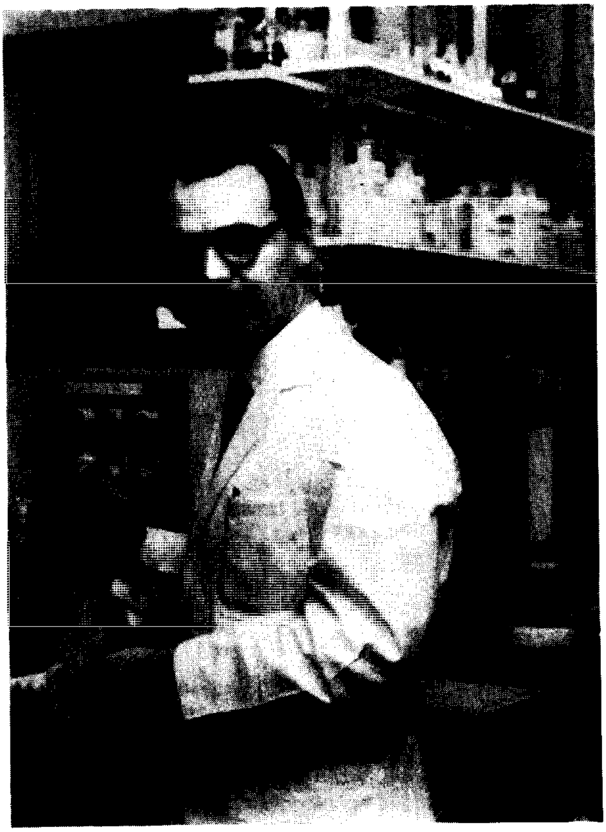
ИЗМЕНЕНИЯ ПРОГРАММЫ SCOGS ДЛЯ ЭЛЕКТРОНОВЫЧИСЛИТЕЛЬНОЙ МАШИНЫ:

W. A. E. McBryde and J. L. McCourt, *Talanta*, 1972, **19**, 1486.

Резюме—Программа SCOGS изменена с целью применения на все константы равновесия включающие перенос протонов, в форме частного концентрации. Получены значительные экономии времени при использовании компилятора FORTRAИ Н.

ADVISORY BOARD OF TALANTA

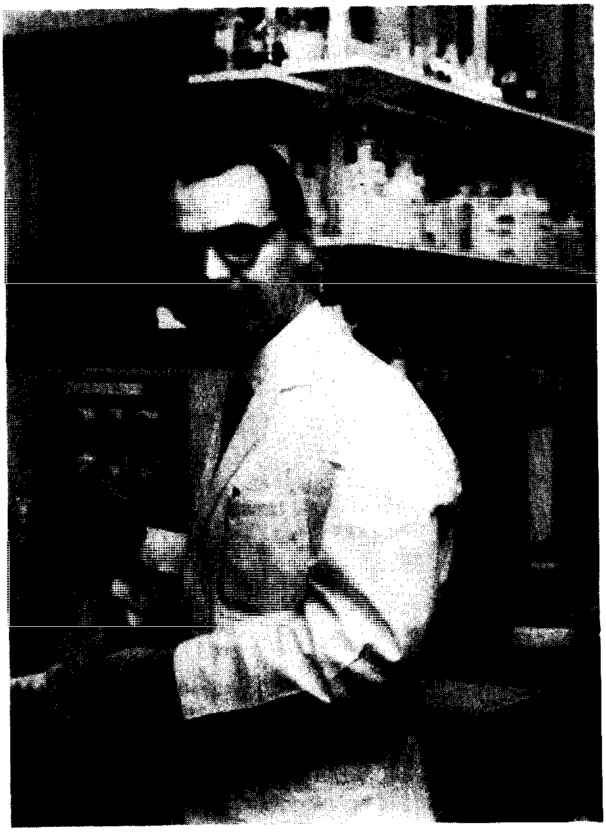
The Editorial Board and Publishers of *Talanta* take pleasure in welcoming Professor GILLIS JOHANSSON to the Advisory Board of the journal.



PROFESSOR JOHANSSON was born in 1931, and graduated Ph.D. at Lund in 1965. In 1967 he was appointed the first professor in analytical chemistry in Umeå University, where he is now also Dean of the Faculty of Science. He is also a member of the Swedish National Committee for Chemistry. His scientific interests include electrochemical methods of analysis, ion-selective electrodes and atomic-absorption spectroscopy by the graphite furnace technique. He has written 30 papers and a book (on operational amplifiers). Professor Johansson is married and has two children.

ADVISORY BOARD OF TALANTA

The Editorial Board and Publishers of *Talanta* take pleasure in welcoming Professor GILLIS JOHANSSON to the Advisory Board of the journal.



PROFESSOR JOHANSSON was born in 1931, and graduated Ph.D. at Lund in 1965. In 1967 he was appointed the first professor in analytical chemistry in Umeå University, where he is now also Dean of the Faculty of Science. He is also a member of the Swedish National Committee for Chemistry. His scientific interests include electrochemical methods of analysis, ion-selective electrodes and atomic-absorption spectroscopy by the graphite furnace technique. He has written 30 papers and a book (on operational amplifiers). Professor Johansson is married and has two children.

Reprints of the following reviews published in Talanta are available from Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, or Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

1 **Precipitation of Metal Chelates from Homogeneous Solution** by F. H. Firsching

2 **Recent Developments in the Ring Oven Technique** by H. Weisz

3 **Adsorption Indicators in Precipitation Titrations** by R. C. Mehrotra and K. N. Tandon

4 **Radiometric Titrations** by T. Braun and J. Tölgyessy

5 **Recent Uses of Liquid Ion Exchangers in Inorganic Analysis** by H. Green

6 **Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry** by B. D. Flockhart and R. C. Pink

7 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum** by F. E. Beamish

8 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold** by F. E. Beamish

9 **Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals** by R. Přibil

10 **Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique** by F. Girardi

11 **Separation of Transplutonium Elements** by J. Starý

12 **Differential Spectrophotometry** by G. Svehla

13 **A Critical Review of Gravimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

14 **A Critical Review of Titrimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

15 **Present State of Complexometry—II: Determination of Bivalent Metals** by R. Přibil

Reprints of Talanta Reviews

As the volume of scientific literature grows, reviews provide one of the best means of keeping abreast with recent developments. Talanta has commissioned a series of comprehensive and critical reviews of topics of current interest to analytical chemists; many of these reviews will also be of value to chemists in general and to other scientists. Talanta Reviews are intended primarily to introduce the non-specialist to a subject about which he previously knew little, but they may also help the specialist fill gaps in his knowledge of his own field or illuminate the subject from a new angle.

16 **Derivatography: A Complex Method in Thermal Analysis**
by F. Paulik, J. Paulik and L. Erdey

17 **Potassium Dichromate as an Oxidimetric Reagent**
by G. Gopala Rao

18 **Newer Acylation Methods for the Determination of Organic Hydroxyl and Amino Compounds** by N. K. Mathur

19 **A Critical Review of Neutron Activation and Tracer Methods for the Determination of the Noble Metals**
by F. E. Beamish, K. S. Chung and A. Chow

20 **Process Gas Chromatography** by C. S. F. Pine

21 **Present State of Complexometry—III and IV: Determination of Univalent Metals and Determination of Rare Earths** by R. Přibil

22 **A Critical Review of Methods of Isolating and Separating the Noble Metals—II: Ion Exchange and Solvent Extraction**
by F. E. Beamish

23 **A Critical Review of Methods of Isolating and Separating the Noble Metals—III: Chromatography, Precipitation and Fire Assay** by F. E. Beamish

24 **Complexation Reactions of Dithiocarbamates**
by A. Hulanicki

25 **Polarographic Behaviour of Metal Chelates of *o,o′*-Dihydroxyazo Dyes** by G. W. Latimer, Jr.

26 **Characteristic Metal-Halogen Vibrational Frequencies of Complexes with Bivalent Metal Halides** by R. H. Nuttall

27 **Amplification Reactions** by R. Belcher

28 **Ternary Complexes in Analytical Chemistry**
by A. K. Babko

29 **Determination of Antioxidants in Polymeric Materials**
by D. A. Wheeler

30 **A Critical Review of Atomic Absorption, Spectrochemical, and X-ray Fluorescence Methods for the Determination of the Noble Metals—II**
by F. E. Beamish, C. L. Lewis and J. C. Van Loon

31 **Applications of Digital Computers in Analytical Chemistry—I** by C. W. Childs, P. S. Hallman and D. D. Perrin

32 **Applications of Digital Computers in Analytical Chemistry—II** by C. W. Childs, P. S. Hallman and D. D. Perrin

33 **Fluorescence Analysis in Air Pollution Research**
by E. Sawicki

34 **Radioactive Kryptonates and Their Uses in Chemical Analysis** by J. Tölgyessy and Š. Varga

35 **Quantitative Analysis in Pharmacy and Pharmaceutical Chemistry by Nuclear Magnetic Resonance Spectroscopy**
by D. M. Rackham

36 **Recent Developments in Substoichiometric Analysis**
by J. Starý and J. Růžička

continued overleaf

37 **Analytical and Experimental Aspects of Molecular-Sieve Chromatography**
by D. M. W. Anderson, I. C. M. Dea and A. Hendrie

38 **Use of Basic Dyes in the Determination of Anions, Particularly as a Means of Determining Antimony, Thallium, and Gallium**
by A. G. Fogg, C. Burgess and D. Thorburn Burns

39 **Organic Analysis by Luminescence Methods**
by J. Bartos and M. Pesez

40 **Synthetic Inorganic Ion-Exchangers—I. Hydrous Oxides and Acetic Salts of Multivalent Metals**
by V. Veselý and V. Pekárek

41 **Analytical Mass Spectrometry**
by J. R. Majer

£0·35 or $1 each

ORDER FORM

Date.............

(Customers in America and Canada should return this form to the New York address)

Please send ......copy/copies of the following Talanta Reviews (please list numbers)

....

for which I enclose £................ $................

Name..

Address ....

....

....

Pergamon Press

Headington Hill Hall
Oxford, England

Maxwell House,
Fairview Park, Elmsford,
New York 10523, U.S.A.

Reprints of the following reviews published in Talanta are available from Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England, or Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.

1 **Precipitation of Metal Chelates from Homogeneous Solution** by F. H. Firsching

2 **Recent Developments in the Ring Oven Technique** by H. Weisz

3 **Adsorption Indicators in Precipitation Titrations** by R. C. Mehrotra and K. N. Tandon

4 **Radiometric Titrations** by T. Braun and J. Tölgyessy

5 **Recent Uses of Liquid Ion Exchangers in Inorganic Analysis** by H. Green

6 **Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry** by B. D. Flockhart and R. C. Pink

7 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum** by F. E. Beamish

8 **A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold** by F. E. Beamish

9 **Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals** by R. Přibil

10 **Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique** by F. Girardi

11 **Separation of Transplutonium Elements** by J. Starý

12 **Differential Spectrophotometry** by G. Svehla

13 **A Critical Review of Gravimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

14 **A Critical Review of Titrimetric Methods for Determination of the Noble Metals—II** by F. E. Beamish

15 **Present State of Complexometry—II: Determination of Bivalent Metals** by R. Přibil

Reprints of Talanta Reviews

As the volume of scientific literature grows, reviews provide one of the best means of keeping abreast with recent developments. Talanta has commissioned a series of comprehensive and critical reviews of topics of current interest to analytical chemists; many of these reviews will also be of value to chemists in general and to other scientists. Talanta Reviews are intended primarily to introduce the non-specialist to a subject about which he previously knew little, but they may also help the specialist fill gaps in his knowledge of his own field or illuminate the subject from a new angle.

16 **Derivatography: A Complex Method in Thermal Analysis**
by F. Paulik, J. Paulik and L. Erdey

17 **Potassium Dichromate as an Oxidimetric Reagent**
by G. Gopala Rao

18 **Newer Acylation Methods for the Determination of Organic Hydroxyl and Amino Compounds** by N. K. Mathur

19 **A Critical Review of Neutron Activation and Tracer Methods for the Determination of the Noble Metals**
by F. E. Beamish, K. S. Chung and A. Chow

20 **Process Gas Chromatography** by C. S. F. Pine

21 **Present State of Complexometry—III and IV: Determination of Univalent Metals and Determination of Rare Earths** by R. Přibil

22 **A Critical Review of Methods of Isolating and Separating the Noble Metals—II: Ion Exchange and Solvent Extraction**
by F. E. Beamish

23 **A Critical Review of Methods of Isolating and Separating the Noble Metals—III: Chromatography, Precipitation and Fire Assay** by F. E. Beamish

24 **Complexation Reactions of Dithiocarbamates**
by A. Hulanicki

25 **Polarographic Behaviour of Metal Chelates of *o,o′*-Dihydroxyazo Dyes** by G. W. Latimer, Jr.

26 **Characteristic Metal-Halogen Vibrational Frequencies of Complexes with Bivalent Metal Halides** by R. H. Nuttall

27 **Amplification Reactions** by R. Belcher

28 **Ternary Complexes in Analytical Chemistry**
by A. K. Babko

29 **Determination of Antioxidants in Polymeric Materials**
by D. A. Wheeler

30 **A Critical Review of Atomic Absorption, Spectrochemical, and X-ray Fluorescence Methods for the Determination of the Noble Metals—II**
by F. E. Beamish, C. L. Lewis and J. C. Van Loon

31 **Applications of Digital Computers in Analytical Chemistry—I** by C. W. Childs, P. S. Hallman and D. D. Perrin

32 **Applications of Digital Computers in Analytical Chemistry—II** by C. W. Childs, P. S. Hallman and D. D. Perrin

33 **Fluorescence Analysis in Air Pollution Research**
by E. Sawicki

34 **Radioactive Kryptonates and Their Uses in Chemical Analysis** by J. Tölgyessy and Š. Varga

35 **Quantitative Analysis in Pharmacy and Pharmaceutical Chemistry by Nuclear Magnetic Resonance Spectroscopy**
by D. M. Rackham

36 **Recent Developments in Substoichiometric Analysis**
by J. Starý and J. Růžička

continued overleaf

Talanta, 1972, Vol. 19, pp. 1 to 6. Pergamon Perss. Printed in Northernlreland

REMOVAL OF GRAPHITE BY OXIDATION WITH PERCHLORIC ACID PLUS PERIODIC ACID

INAPPLICABILITY TO THE SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEEL

JAMES A. GAUNT and HARVEY DIEHL
Department of Chemistry, Iowa State University, Ames, Iowa, 50010, U.S.A.

(*Received* 2 *July* 1971. *Accepted* 4 *October* 1971)

Summary—An attempt has been made to improve the Willard and Greathouse periodate method for the determination of manganese in high-carbon steel and cast iron by oxidizing the graphite with periodic acid in the presence of perchloric acid and phosphoric acid. Graphite is rapidly oxidized at 150° by this mixture but manganese is lost by volatilization as the heptoxide and decomposition of the latter on hot surfaces to manganese dioxide. No way was found for either the quantitative removal and recovery of manganese by volatilization or for quantitative return to the main solution. The spectrophotometric determination of manganese in the supernatant liquid after allowing graphite to settle yields imprecise but not wholly unacceptable results; for the highest accuracy, graphite should be removed along with silica following dehydration of the latter with perchloric acid.

MANGANESE in steel is commonly determined spectrophotometrically as permanganate following oxidation of the manganese by periodic acid, a procedure devised by Willard and Greathouse[1] in 1917 and subsequently adopted by the ASTM[2] and other organizations publishing official methods of analysis. In the Willard and Greathouse procedure carbon is oxidized by boiling with persulphate after dissolution of the steel in sulphuric acid. This procedure works well for most steels but fails with high-carbon steels and cast irons in which an appreciable amount of the carbon is present as graphitic carbon. In the present work, a procedure has been devised for destroying graphitic carbon by oxidation with periodic acid in a perchloric acid–phosphoric acid medium. Curiously, the procedure fails as a method for the spectrophotometric determination of manganese owing to the volatility of manganese in the septavalent state.

The use of a mixture of perchloric acid and periodic acid for the wet oxidation of organic matter was described by Smith and Diehl.[3] The mixture was applied by Spielholtz *et al.*[4] to the wet oxidation of coal before the determination of minor constituents, and again by Spielholtz *et al.*,[4] with more careful control of the concentration of perchloric acid and thus of the boiling temperature, to the destruction of carbon in coal, leaving spores unchanged for isolation for studies in stratigraphy. Periodic acid is used for the cleavage of the bond joining two carbon atoms each of which carries a functional group, the attack presumably involving the temporary formation of a five-membered ring involving iodine. The flat, hexagonal arrangement of carbon in graphite provides for rapid attack by periodic acid, which is in fact the only agent which attacks it with speed.

The volatility of manganese in the septavalent state has been noted earlier. Willard and Filson[5] observed it when developing the determination of chromium in steel by volatilization of chromyl chloride by passing chlorine and hydrogen chloride into a perchloric acid solution of a steel. Again, the volatility was observed by Strickland

and Spicer[6] who attempted to develop a method for the separation of manganese based on this phenomenon.

In the present work, the optimum conditions for the oxidation of graphite with periodic acid have been established and attempts have been made to adapt the oxidation to the spectrophotometric determination of manganese in steel and cast iron. The latter effort failed owing to the volatility of manganese heptoxide and its decomposition in the vapour phase to manganese dioxide. In a supplemental study it has also been shown that suspended particles of graphite interfere seriously in the spectrophotometric determination of manganese and must be removed by filtration.

Oxidation of graphitic carbon

Most steels contain less than 2% carbon and this carbon, predominantly iron carbide, is readily oxidized by hot perchloric acid. Carbon obtained on dissolving high-carbon steel or cast iron—the graphite and presumably some of the interstitial carbon—is not destroyed by boiling with concentrated perchloric acid, that is, at 203°. Molybdenum, chromium, vanadium and cerium, materials which catalyse the oxidation of nylon, 8-hydroxyquinoline, 1,10-phenanthroline and other recalcitrant heterocyclic nitrogen compounds by perchloric acid, are not effective in the oxidation of graphite.

After dissolution of a steel in a mixture of nitric acid, perchloric acid and water (1:1:1), graphite present is oxidized rapidly by the addition of sodium periodate. However, during the oxidation there is formed a yellow precipitate which cannot be dissolved by heating or by increasing the concentration of the acids. This yellow precipitate is extremely insoluble and is formed whether the steel is dissolved in a mixture of nitric and perchloric acids or in perchloric acid alone. It is not formed if phosphoric acid is added to the mixture before the addition of sodium periodate, although once formed it takes a large amount of phosphoric acid and heating to dissolve it. In the final procedure, recommended below, the steel is dissolved in a mixture of the three acids. About 3 min are required for the dissolution of a 1-g sample at a temperature of about 120°. The oxidation is best effected by adding the sodium periodate in increments of 0·1 g and at a temperature of 150–160°. For the oxidation of the graphite in a steel containing 2–3% carbon, 1·5 g of sodium periodate and 20–30 min are required. Addition of the sodium periodate must be made in increments owing to the decomposition of periodic acid in hot perchloric acid.[3] If it is added in one portion oxidation is incomplete and more periodate is required.

Recommended procedure for the dissolution of steel and oxidation of carbon

To a sample of steel or cast iron in a 250-ml flask add 50 ml of a mixture of two volumes of 70% perchloric acid, one volume of 70% nitric acid and two volumes of 85% phosphoric acid. Heat to boiling and after the sample has dissolved except for carbonaceous material and silica, continue heating to expel nitric acid and oxides of nitrogen. When the temperature reaches 150–160° add 0·1-g portions (preferably in the form of pellets) of sodium periodate at intervals of 4–5 min, continuing until all of the graphite has been removed.

Formation of manganese heptoxide and dioxide

During the oxidation of graphite with periodic acid in a boiling perchloric acid solution, small droplets of pink liquid formed on the upper walls of the reaction vessel where reflux was occurring. The colour of this liquid was that of the permanganate ion. This pink liquid also formed on a microscope slide held about an inch above the mouth of the flask, indicating that it was being formed by condensation from the vapour and not by spray from the boiling solution. It was thus apparent also that a considerable amount of manganese was being carried from the flask. It was noted further that during the oxidation a brown solid was deposited on the upper walls of the reaction vessel. This deposit was not soluble in hot concentrated perchloric acid and remained on the glassware after the oxidation of graphite was complete; it was soluble in warm hydrochloric acid, and the resulting solution, when treated with periodate, yielded the characteristic colour of permanganate.

It thus became apparent that manganese is oxidized to the septavalent state by periodic acid in hot perchloric acid solution and is volatilized as the heptoxide which condenses in the refluxing liquid to form permanganic acid. It was apparent also that on contact with the hot, dry, upper walls of the reaction vessel manganese heptoxide was decomposed to manganese dioxide. The reactions are

$$5H_5IO_6 + 2Mn^{2+} = Mn_2O_7 + 5HIO_3 + 4H^+ + 8H_2O$$

$$2Mn_2O_7 = 4MnO_2 + 3O_2.$$

That the decomposition of manganese occurred on contact of vapour and the hot wall was further demonstrated by an experiment in which the upper part of the flask was cooled by a water jacket. Manganese was deposited in the border area between the cooled upper walls and the boiling perchloric acid solution and on the exposed part of a sealed-in thermometer well.

Attempts to retain and recover manganese heptoxide and dioxide

The escape of manganese heptoxide was easily prevented by the use of a reflux condenser attached by a ground-glass joint to the flask in which the dissolution and oxidation reactions were carried out. Preventing the formation of manganese dioxide or recovering it quantitatively, however, presented a more formidable problem and one which was not solved in satisfactory fashion.

The possibility of volatilizing all of the manganese from the sample and of collecting it for measurement is attractive. The Bethge apparatus,[7] [8] designed for the retention of volatile materials during the wet oxidation of organic matter by digestion with perchloric acid, appeared ideal for such an experiment. In the Bethge apparatus vapour from the reaction vessel travels up a by-pass into the condenser and reflux is returned to a sump, in the intermediate chamber, from which it can be either returned to the main reaction or withdrawn.

A series of experiments was made with manganese steels and perchloric acid–periodic acid mixtures, the temperature being raised slowly from 60° to 204°. Only small amounts of manganese were obtained in the condensate as judged by the appearance of permanganate colour. The permanganate colour disappeared quickly as it entered the condensate, undoubtedly because of reaction with hydrochloric acid always produced during the boiling of perchloric acid. More manganese was obtained when the temperature was raised rapidly but quantitative distillation was never obtained. Nor did experiments with simpler, conventional distillation apparatus give better results. Iron as well as manganese was found in the distillates in these experiments.

Dissolving the deposit of manganese dioxide from the walls of the flask proved easy with hydrochloric acid plus bisulphite, but the resulting solution was not satisfactory for the spectrophotometric determination of manganese; the hydrochloric acid caused the permanganate (formed by periodate oxidation as in the usual Willard and Greathouse procedure) to be unstable.

Somewhat better results were obtained when the main solution, containing the major part of the manganese was transferred to a volumetric flask after oxidation of the graphite and the deposit of manganese dioxide on the upper walls of the reaction vessel was dissolved by treatment with a mixture of equal volumes of sulphuric acid and phosphoric acid plus sodium bisulphite. In 5 min or so the manganese dioxide was dissolved and sulphur dioxide expelled. This solution was added to the main solution and the usual periodate oxidation of the manganese to permanganate and spectrophotometric measurement was then applied. The results were not good; on NBS 122D, Cast Iron, the results were consistently low and scattered: found, 0·453, 0·478, 0·476, 0·463%, NBS value: 0·504% manganese.

The cumbersome and time-consuming manipulations required to retain the manganese heptoxide and to recover the manganese dioxide make the periodic acid oxidation of graphite unacceptable for the spectrophotometric determination of manganese in steel or cast iron.

Interference of graphite in the spectrophotometric determination of manganese

Having failed to find a method of destroying graphite without loss of manganese, we assessed the effect of carrying out the spectrophotometric determination of manganese in the presence of the graphite. Basically, this study involved a comparison of two procedures, one in which the graphite was simply allowed to settle and the determination made on the clear supernatant liquid, and a second in which the graphite was removed by filtration and the determination made on the filtrate. The final procedures used are given in the next two paragraphs.

Graphite allowed to settle. A sample containing approximately 2–3 mg of manganese was dissolved in 50 ml of a mixture of concentrated perchloric, nitric, and phosphoric acids (2:1:2). The mixture was heated until the nitric acid fumes had been driven off. The solution was then cooled and then diluted with 100 ml of water. About 1 g of sodium periodate was added. The solution was heated almost to boiling to oxidize manganese(II) to permanganate. The solution was cooled, transferred to a volumetric flask, and diluted to exactly 250 ml with water. The particles of graphite were then allowed to settle and an aliquot of the supernatant liquid was carefully withdrawn for the spectrophotometric measurement. A calibration curve was made from measurements on dilutions of a stock solution of known concentrations of manganese(II) prepared from electrolytic manganese metal, 99·75% pure, treated in the same manner. The purity of the electrolytic manganese was established by comparison with primary-standard manganous oxalate dihydrate.[9]

Removal of graphite by filtration. A sample containing approximately 2–3 mg of manganese was dissolved in 50 ml of the acid mixture. The mixture was heated until nitric oxide fumes had been expelled and perchloric acid was refluxing smoothly on the lower half of the walls of the flask. The mixture was held at this temperature for 20 min to dehydrate silica. The solution was cooled and then diluted with 100 ml of water. The solution was filtered through a coarse filter paper (Whatman No. 41). To the filtrate was added 1 g of sodium periodate. The solution was heated almost to boiling to oxidize manganese(II) to permanganate. The solution was cooled, transferred to a volumetric flask, and diluted to exactly 250 ml. The absorbance was then measured. A calibration curve was made as before.

RESULTS AND DISCUSSION

The studies were made on two samples of cast iron of the National Bureau of Standards, NBS 342 and NBS 122D. The results are shown in Table I. The average of seven determinations of the manganese in NBS 342 by the settling procedure was slightly lower than the NBS value and the precision was poor. The average of seven determinations on NBS 122D was slightly higher than the NBS value and again the precision was poor.

TABLE I.—DETERMINATION OF MANGANESE IN CAST IRON AND STEEL: EFFECT OF REMOVAL OF GRAPHITE BY FILTRATION

Sample	NBS values		Procedure	Mn average %	Manganese found		Relative standard deviation *ppt*
	Carbon %	Manganese %			Number of determinations	Standard deviation %	
NBS 342 Nodular Cast Iron	2·45	0·369	Settling	0·361	9	0·017	47
			Filtration	0·379	6	0·004	11
NBS 122D Cast Iron	3·28	0·504	Settling	0·578	6	0·013	23
			Filtration	0·523	6	0·008	15
NBS 51 Electric Steel	1·29	0·271	Settling	0·282	6	0·002	7
NBS 16D Basic Open Hearth Steel	1·01	0·439	Settling	0·466	7	0·008	7
NBS 14D Basic Open Hearth Steel	0·841	0·399	Settling	0·401	8	0·003	7

On the other hand, accuracy and precision were much better when the graphite was removed by filtration. The precision was from two to five times better than that of the settling method.

Several samples of steel were analysed by the settling procedure. Although these samples contained up to 1·2% carbon, no graphite and very little silica remained after dissolution. Excellent precision was obtained and the values were close to those of the NBS.

For results of the highest accuracy in the determination of manganese, graphite should be removed before the spectrophotometric measurement is made.

Zusammenfassung—Es wurde versucht, die Perjodatmethode von Willard und Greathouse zur Bestimmung von Mangan in kohlenstoffreichem Stahl und Gußeisen durch Oxidation des Graphits mit Überjodsäure in Gegenwart von Überchlorsäure und Phosphorsäure zu verbessern. Graphit wird von diesem Gemisch bei 150° rasch oxidiert, aber Mangan geht als flüchtiges Heptoxid verloren; dieses zersetzt sich an heißen Oberflächen zu Mangandioxid. Es wurde kein Weg gefunden, das Mangan entweder quantitativ zu verflüchtigen und wieder aufzufangen oder es quantitativ in die Hauptlösung zurückzuführen. Die spektrophotometrische Bestimmung von Mangan in der Lösung nach Absitzen des Graphits gibt ungenaue, wenn auch nicht völig unbrauchbare Ergebnisse; um die höchste Genauigkeit zu erzielen, sollte Graphit zusammen mit der Kieselsäure entfernt werden, nachdem diese mit Überchlorsäure entwässert wurde.

Résumé—On a tenté d'améliorer la technique de Willard et Greathouse au periodate pour le dosage du manganèse dans l'acier à haute teneur en carbone et dans la fonte en oxydant le graphite par l'acide periodique en la présence d'acide perchlorique et d'acide phosphorique. Le graphite est oxydé rapidement à 150° par ce mélange, mais il y a perte de manganèse par volatilisation à l'état d'heptoxyde et décomposition de ce dernier sur les surfaces chaudes en bioxyde de manganèse. On n'a pas trouvé de voie, soit pour l'élimination et la récupération quantitatives du manganèse par volatilisation, soit pour le retour quantitatif dans la solution principale. Le dosage spectrophotométrique du manganèse dans le liquide surnageant après que le graphite se soit déposé donne des résultats imprécis mais non absolument inacceptables; pour avoir la meilleure précision, le graphite doit être séparé en même temps que la silice après la déshydratation de celle-ci par l'acide perchlorique.

REFERENCES

1. H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, 1917, **39**, 2366.
2. *1970 Annual Book of ASTM Standards*, Part 32, p. 833.
3. G. F. Smith and H. Diehl, *Talanta*, 1960, **4**, 185.
4. G. I. Spielholtz, L. A. Thomas, and H. Diehl, *Micropaleontology*, 1962, **8**, 109.
5. M. Filson, *Ph.D. Thesis.* University of Michigan, Ann Arbor, Michigan, 1935.
6. J. D. H. Strickland and G. Spicer, *Anal. Chim. Acta*, 1949, **3**, 543.
7. P. O. Bethge, *Anal. Chim. Acta*, 1953, **10**, 317.
8. H. Diehl and G. F. Smith, *Proc. Intern. Symp. Microchemistry, Birmingham, 1958*, p. 41. Pergamon, Oxford, 1960.
9. J. Knoeck and H. Diehl, *Talanta*, 1967, **14**, 1085.

Talanta, 1972, Vol. 19, pp. vii to viii. Pergamon Press. Printed in Northern Ireland

NOTICES

SECOND AUSTRALIAN SYMPOSIUM ON ANALYTICAL CHEMISTRY

The Analytical Chemistry Division of the Royal Australian Chemical Institute will be holding its Second Symposium on Analytical Chemistry at the University of New South Wales, Kensington, on 14–18 May 1973.

Papers dealing with all aspects of analytical chemistry, including biochemical, clinical, mineral, metallurgical, environmental, modern instrumental, pharmaceutical, educational, and data handling and processing will be accepted.

Further information may be obtained from the Hon. Secretary:

Mr. L. S. Dale,
Australian Atomic Energy Commission,
Research Establishment
Private Mail Bag P.O. Sutherland,
N.S.W. 2232 Australia.

INTERNATIONAL SYMPOSIUM ON MICROCHEMICAL TECHNIQUES—1973

"Progress and Projections for Microchemistry," will be the general theme for The International Symposium on Microchemical Techniques—1973. The symposium will be held at The Pennsylvania State University, University Park, Pennsylvania, on 19–24 August 1973 and will be conducted by The American Microchemical Society, with the sponsorship of the International Union of Pure and Applied Chemistry.

The scientific programme will consist of sessions dedicated to topics of current interest, general papers, discussion groups, practical demonstrations, an equipment exhibit, and will also include a number of instructional workshop sessions. Special sessions will be included on such topics as:

Automated Elemental Analyzers—Ten years Later
Computers in Elemental Analysis
Organic Elemental Analysis: New Methods and Equipment
Environmental Microanalysis: New Sensors and Techniques
Microelectrodes
Forensic Analysis: Narcotics and Drugs of Abuse
Organic Functional Group Analysis: New Directions
Electroanalytical Advances, including Ion Selective Electrodes
Microscale Separations: Advances in Techniques and Methods
Standards and Standardization for Microchemistry and Microanalysis
Trace Analysis: Advances in Organic and Inorganic Analysis
New Techniques in Microchemistry

Persons interested in presenting a paper under any of the above topics, or a paper on the general topic of microchemistry, should submit their paper to:

Mr. Howard J. Francis, Jr.
Pennwalt Corporation
900 First Avenue
King of Prussia, Pennsylvania 19406

Included in the program of scientific presentations will be classroom workshops on the topics of:
Applications of Ion Selective Electrodes
Theory and Applications of thermal Methods of Analysis

1973 PITTSBURGH CONFERENCE

The twenty-fourth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy will be held at the Cleveland Convention Center, Cleveland, Ohio, U.S.A., 5–9 March 1973. An estimated 350 papers on all phases of Analytical Chemistry and Spectroscopy will be presented. Symposia on the following subjects are now being arranged.

1. LIQUID CHROMATOGRAPHY—Analytical Bridge to Spectroscopy.
2. THREE DIMENSIONAL MICROCOMPOSITIONAL ANALYSIS: The Advent of Ion Probe Mass Spectrometry.
3. INDUSTRIAL APPLICATIONS OF ^{13}C NMR.
4. FORENSIC SCIENCE.
5. WOMEN IN MASS SPECTROMETRY.
6. INDUSTRIAL RESEARCH—Is it Worth It?
7. GUIDELINES FOR DEFINING AND IMPLEMENTING THE COMPUTERIZED LABORATORY SYSTEM (ASTM).
8. THE ANALYSIS OF SLAGS AND RELATED OXIDE-TYPE MATERIALS (ASTM).
9. COBLENTZ SOCIETY AWARD SYMPOSIUM.
10. SPECTROSCOPY SOCIETY OF PITTSBURGH AWARD SYMPOSIUM

In addition to the programme of technical papers, more than 250 companies, both foreign and domestic, will be represented at the exposition of Modern Laboratory Equipment, the largest exposition of analytical instrumentation and related materials in the world.

For further information apply to

H. L. Retcofsky
1973 Pittsburgh Conference
U.S. Bureau of Mines
4800 Forbes Avenue
Pittsburgh, Pa. 15213, U.S.A.

INTERNATIONAL SYMPOSIUM ON LIQUID SCINTILLATION COUNTING

Following last year's very successful venture the Radiochemical Methods Group of the Society for Analytical Chemistry/Analytical Division, Chemical Society propose holding a second International Symposium on Liquid Scintillation Counting. It will be held at the Hotel Metropole, Brighton, England, on 3–6 September 1973. An exhibition of scintillation counters, scintillators, and associated equipment will be held in conjunction with the scientific programme.

Persons wishing to present a contribution to this symposium and firms wishing to take part in the exhibition should write for further details to

Mr. M.A. Crook,
The Society for Analytical Chemistry,
9/10 Savile Row,
London W1X 1AF.

SUMMARIES FOR CARD INDEXES

Extreme trace analysis of the elements—I. Methods and problems of sample treatment, separation and enrichment: GÜNTHER TÖLG, *Talanta*, 1972, **19**, 1489. (Max-Planck-Institut für Metallforschung, Laboratorium für Reinstoffe, 7070-Schwäbisch Gmünd, Katherinenstraße 17, B.R.D.)

Summary—In the determination of elements in the ppM range in inorganic and organic matrices, solution techniques are useful because they simplify calibration problems and improve the limit of detection. The author reviews, in the light of his own experience, some 350 publications concerned with methods for the preparation and dissolution of samples and for the isolation of trace elements before their determination. The errors in these methods, made more difficult to reduce because of the additional operations required, are compared with those associated with the more direct methods.

Determination of water: CLIFFORD HARRIS, *Talanta*, 1972, **19**, 1523. (88 Charlton Road, Keynsham, Nr. Bristol, U.K.)

Summary—The complexity of the subject and the problems involved in the estimation of water in the many materials required to be tested are explained. The various methods available are classified, their techniques summarized, and their applications and limitations indicated. In many materials the determination of absolute moisture is impossible and a compromise must be accepted. Trade and industry require rapid results for many processes and products, and optical or electronic methods are increasingly used in conjunction with reference methods. For official purposes the method of determination must be agreed and stated in detail. More progress in international standardization is very desirable.

Nuclear magnetic resonance analysis of pharmaceuticals—VII. Determination of aminophylline in tablets: JOHN W. TURCZAN, BRUCE A. GOLDWITZ and JAMES J. NELSON, *Talanta*, 1972, **19**, 1549. (Food and Drug Administration, U.S. Department of Health, Education and Welfare, 850, Third Avenue, Brooklyn, New York 11232.)

Summary—An NMR procedure is described by which theophylline and ethylenediamine are simultaneously determined in aminophylline tablets. t-Butyl alcohol was chosen as the internal standard and 4% ammonia–0.3% potassium cyanide in deuterium oxide was the solvent. The solvent system was selected to deal with the problems of solubility of the theophylline, overlapping of the components' resonance signals, and potential interference from metal impurities. Known standard and commercial preparations were determined and the results compared with those obtained by alternative procedures. The technique, when applied to the determination of aminophylline in tablets, is rapid, simple and specific and has an error of 1–2%.

КРАЙНЫЙ СЛЕДОВЫЙ АНАЛИЗ ЭЛЕМЕНТОВ—I. МЕТОДЫ И ПРОБЛЕМЫ ОБРАБОТКИ, РАЗДЕЛЕНИЯ И ОБОГАЩЕНИЯ ПРОБЫ:

G. Tölg, *Talanta*, 1972, **19**, 1489.

Резюме—В определении элементов в области частей на миллион в неорганических и органических матрицах, методы пользующиеся растворами оказалися полезными потому что упрощают проблемы калибровки и улучшают предел чувствительности. Учитывая собственный опыт, автор приводит обзор 350 публикаций касающихся методов приготовления и растворения образцов и выделения следов элементов перед их определением. Ошибки этих методов, которые трудно избежать из-за надобности применения дополнительных операций, сравнены с ошибками более непосредственных методов.

ОПРЕДЕЛЕНИЕ ВОДЫ:

Clifford Harris, *Talanta*, 1972, **19**, 1523.

Резюме—Рассмотрена сложность вопроса и проблемы связанные с определением воды в многочисленных исследуемых веществах. Сделана классификация имеющихся методов, приведены тезисы их методики и указано их применение и недостатки. В ряде материалах невозможно определять абсолютную влагу и надо придти к компромиссу. В торговле и промышленности изыскуют быстрые результаты для многих процессов и продуктов, следоватольно применяют во всё возрастающем размере оптиуеские или электронные методы в связы с стандартными методами. Для официальных целей надо привести детальное описание методики и соглашаться с методом. Развить международную стандартизацию очень желательно.

АНАЛИЗ ФАРМАЦЕВТИЧЕСКИХ ПРЕПАРАТОВ МЕТОДОМ ЯДЕРНОГО МАГНИТНОГО РЕЗОНАНСА—VII. ОПРЕДЕЛЕНИЕ АМИНОФИЛЛИНА В ТАБЛЕТКАХ:

John W. Turczan, Bruce A. Goldwitz and James J. Nelson, *Talanta*, 1972, **19**, 1549.

Резюме—Описана методика ЯМР для одновременного определения теофиллина и этилендиамина в таблетках аминофиллина. В качестве внутренного стандарта отобран трет-бутиловый спирт, а смесь 4% аммиака и 0,3% цианида калия в окиси дейтерия в качестве растворителя. Состав растворителя отобран с целью решить проблемы растворения теофиллина, избежать перекрытие резонансных сигналов компонентов и устранять мешающее действие примесей металлов. Методика испытана на стандартных и коммерческих преларатах и результаты сравнены с результатами полученными другими методами. Применена в определении аминофиллина, методика является быстрой, несложной и специфической, а ошибка метода—1–2%.

The decomposition of hypobromite solutions: N. VELGHE and A. CLAEYS, *Talanta*, 1972, **19**, 1555. (Laboratory of Analytical Chemistry, Faculty of Pharmacy, University of Ghent, Ghent, Belgium.)

Summary—The stability of 10^{-1}–$10^{-3}N$ hypobromite solutions, stored in brown or colourless bottles at room temperature, has been investigated. A reaction mechanism of decomposition has been proposed and some practical conclusions have been drawn concerning the optimal method of preparation and the required frequency of control of hypobromite solutions used as an analytical reagent.

Quantitative reflectometry—I. Principles and scope: DAVID KEALEY, *Talanta*, 1972, **19**, 1563. (School of Chemical Science and Technology, Kingston Polytechnic, Kingston-upon-Thames, Surrey, U.K.).

Summary—The technique of quantitative reflectometry is critically investigated, the model being the quantitative determination of nickel in aqueous media. Direct reflectance measurements can be made on commercially available nickel test-strips which develop a pink or red colour in the presence of nickel ions. Relative precisions at the 10 and 50 ppm levels are 2.3-3.6%.

Rapid separation and determination of chromium: JAMES S. FRITZ and JOHN P. SICKAFOOSE, *Talanta*, 1972, **19**, 1573. (Ames Laboratory USAEC and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Chromium(III) is oxidized to chromium(VI) at room temperature or by conventional persulphate oxidation. The chromium(VI) is separated from other metal ions by retention on a small anion-exchange column, and then eluted with a perchlorate solution and measured spectrophotometrically with a flow-through cell. The method is rapid, selective and amenable to automation.

Review of the analytical chemistry of melatonin: E. R. COLE and G. CRANK, *Talanta*, 1972, **19**. 1581. (Department of Applied Organic Chemistry, The University of New South Wales, Kensington, 2033, N.S.W., Australia).

Summary—A survey has been made of procedures, chemical and biochemical, for the separation and estimation of melatonin, the active constituent of the pineal gland. In view of the extremely small amounts of material generally present, discussion is built around chromatographic and spectroscopic techniques leading to a comparison with assays based on the skin-blanching effect of the hormone.

РАЗЛОЖЕНИЕ РАСТВОРОВ ГИПОБРОМИТА:

N. Velghe and A. Claeys, *Talanta*, 1972, **19**, 1555.

Резюме—Изучена устойчивость при комнатной температуре содержанных в бурых или неокрашенных склянках 10^{-1} до 10^{-3} N растворов гипобромита. Предложен реакционный механизм разложения и сделаны некоторые практические выводы касающиеся оптимального метода приготовления и нужной частоты контроля растворов гипобромита, использованных в качестве аналитического реагента.

КОЛИЧЕСТВЕННАЯ РЕФЛЕКТОМЕТРИЯ—I. ПРИНЦИПЫ И ОБЛАСТЬ ПРИМЕНЕНИЯ МЕТОДА:

David Kealy, *Talanta*, 1972, **19**, 1563.

Резюме—Критически исследован метод количественной рефлектометрии на примере количественного определения никеля в водных средах. Можно измерять непосредственно коэффициент отражения на коммерческих образцах никеля, на которых проявляется розовая или красная окраска в присутствии ионов никеля. Относительная точность при 10 и 50 ч. на миллион составляет 2,3 и 3,6 %, соответственно.

БЫСТРОЕ ВЫДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ ХРОМА:

James S. Fritz and John P. Sickafoose, *Talanta*, 1972, **19**, 1573.

Резюме—Хром(III) окисляют в хром(VI) при комнатной температуре или обыкновенным методом с помощью персульфата. Хром(VI) отделяют от других ионов металлов абсорбцией на небольшой колонке анионообменника, а его затем элюируют раствором перхлората и измеряют спектрофотометрическим методом, с использованием проточной кюветки. Метод быстрый и селективный и легко поддается автоматизации.

ОБЗОР АНАЛИТИЧЕСКОЙ ХИМИИ МЕЛАТОНИНА:

E. R. Cole and G. Crank, *Talanta*, 1972, **19**, 1581.

Резюме—Сцелан обзор химических и биохимических методик для выделения и определения мелатонина, активного компонента гэпифизы. Принимая во внимание имеющиеся очень небольшие количества материала, главный интерес посвящен хроматографическимии спектроскопическим методам, в сравнении с определением основывающемся на белении кожи этим гормоном.

Mössbauer investigation of iron-aluminium mixed oxides: L. KORECZ, I. KURUCZ, G. MENCZEL, E. PAPP-MOLNÁR, E. PUNGOR and K. BURGER, *Talanta*, 1972, **19**, 1599. (Department of Atomic Physics, Department of Experimental Physics and Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, and Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.)

Summary—Mixed hydroxides of iron and aluminium have been precipitated from solutions containing iron and aluminium salts. The ratio of iron and aluminium was changed from 1:1 to 1:9. The mixed oxides produced by heating the hydroxides have been investigated by the Mössbauer effect. The Mössbauer spectra were composed of two systems of lines: one is due to magnetic splitting produced by α-Fe_2O_3, the other is due to quadrupole splitting (0·45 mm/s) which can be assigned to iron atoms in the lattice of α-Al_2O_3. The role of the anion of the solvated salts has also been investigated.

Coulometric titration of acids in isopropanol—I. A rapid direct method for the determination of carbon in steel: B. METTERS, B. G. COOKSEY and J. M. OTTAWAY, *Talanta*, 1972, **19**, 1605. (Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow, C.1.)

Summary—A new procedure is described for the direct coulometric titration of the carbon dioxide liberated in the high-temperature combustion of steel. The carbon dioxide is absorbed in isopropanol containing 3% of ethanolamine and titrated with 100% titration efficiency with a constant current of 50 mA and spectrophotometric detection of the end-point. The accuracy and precision of the method have been established by the analysis of a wide range of standard steel samples.

Bestimmung des Komplextypus und der Beständigkeitskonstante von dissoziierten Komplexen mit Hilfe transformierter Titrationskurven: J. BORÁK, Z. SLOVÁK and J. FISCHER, *Talanta*, 1972, **19**, 1611. (Forschungsinstitut für reine Chemikalien, Lachema, Brno, Tschechoslowakei.)

Summary—A method is presented for the logarithmic transformation of photometric titration curves, with the aid of which it is possible to differentiate with certainty between mononuclear and polynuclear complexes. The mathematical expressions are derived, and applied to practical examples, leading to unequivocal conclusions. The method suffers from two limitations—over a wide range of concentrations only one complex should be formed, and it must be a relatively weak one.

ИЗУЧЕНИЕ СМЕШАННЫХ ОКИСЕЙ ЖЕЛЕЗА И АЛЮМИНИЯ С ПОМОЩЬЮ ЭФФЕКТА МЕССБАУЕРА:

L. Korecz, I. Kurucz, G. Menczel, E. Papp-Molnár, E. Pungor and K. Burger, *Talanta*, 1972, **19**, 1599.

Резюме—Смешанные гидроокиси железа и алюминия осаждены из растворов, содержащих соли железа и алюминия. Отношение железа и алюминия изменено от 1:1 до 1:9. Смешанные окиси произведенные нагреванием гидроокисей исследованы с помощью эффекта Мессбауера. Спектры Мессбауера составлены из двух систем линий: одна из них появляется в результате расщепления вызванного α-Fe_2O_3, друга—в результате квадрупольного расщепления (0,45 мм/сек) которое можно приписать действию атомов железа в решетке γ—Al_2O_3. Также изучен рольанион а сольватированных солей.

КУЛОНОМЕТРИЧЕСКОЕ ТИТРОВАНИЕ КИСЛОТ В ИЗОПРОПАНОЛЕ—I. БЫСТРЫЙ НЕПОСРЕДСТВЕННЫЙ МЕТОД ОПРЕДЕЛЕНИЯ УГЛЕРОДА В СТАЛИ:

B. Metters, B. G. Cookey, and J. M. Ottaway, *Talanta*, 1972, **19**, 1605.

Резюме—Описана новая методика непосредственного кулонометрического определения двуокиси углерода, выделенного при высокотемпературном сжигании стали. Двуокись углерода поглощают в изопропанол содержащий 3% этаноламина и титруют с 100%-тной эффективностью постоянным током 50 ма с использованием спектрофотометрического обнаружения конца титрования. Определены точность и воспроизводимость метода анализируя ряд эталонных образцов стали.

ОПРЕДЕЛЕНИЕ ТИПА И КОНСТАНТЫ УСТОЙЧИВОСТИ ДИССОЦИИРОВАННЫХ КОМПЛЕКСОВ С ПОМОЩЬЮ ТРАНСФОРМИРОВАННЫХ КРИВЫХ ТИТРОВАНИЯ:

J. Borák, Z. Slovák and J. Fischer, *Talanta*, 1972, **19**, 1611.

Резюме—Предложен метод логарифмической трансформации фотометрических кривых титрования, который позволяет различать одноядерные от многоядерных комплексов. Выведены математические выражения и применены на практические примеры, ведуши к недвусмысленным выводам. Недостатки метода—только один комплекс надо образоваться в широком диапазоне концентраций и этот комплекс должен быть относительно неустойчивый.

Studies of copper(II) sulphide ion-selective electrodes: GILLIS JOHANSSON and KERSTIN EDSTRÖM: *Talanta*, 1972, **19**, 1623. (Department of Analytical Chemistry, University of Umeå, 901 87 Umeå, Sweden.)

Summary—Changes in liquid junction potentials in copper(II) solutions were measured when different reference electrodes were used. The slope and intercept of a calibration curve for a copper-selective electrode will depend on the selection of reference electrode. The condition of the electrode surface of an Orion copper-selective electrode was studied microscopically and the influence of redox potential on stability of the electrode against corrosion is discussed. Oxidizing solutions will produce pits at dislocations in the material and there will be a mixed electrode potential. The slope, stability, and speed of response are much lower when the surface contains pits. Diamond-polishing was shown to improve the electrode significantly.

Indirect atomic-absorption determination of ppM levels of arsenic by combustion of an MIBK extract of arsenomolybdic acid: Y. YAMAMOTO, T. KUMAMARU, Y. HAYASHI, M. KANKE and A. MATSUI, *Talanta*, 1972, **19**, 1633. (Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Hiroshima, Japan.)

Summary—An indirect atomic-absorption method for arsenic has been developed. Arsenic(III) is oxidized to arsenic(V) by iodine, then arsenomolybdic acid is formed and extracted into MIBK from 0·2–1·6*M* hydrochloric acid. Excess of molybdate is scrubbed from the organic phase, and then the molybdenum in the heteropoly acid is determined by its atomic absorption at 313·3 nm. Silicate and phosphate interfere. A procedure is described for determination of ppM levels of arsenic in water.

Determination of small amounts of water with coulometrically generated Karl Fischer reagent: RONALD KARLSSON, *Talanta*, 1972, **19**, 1639. (Department of Analytical Chemistry, Chemical Center, University of Lund, S 220 07 Lund 7, Sweden.)

Summary—A coulometric method for the determination of small amounts of water described in a previous report has been further developed. Improved electronic circuity and a redesigned electrolysis cell have extended the range of determination and decreased the time of analysis. By means of a movable oven specially adapted to the cell, water in solids has also been determined. The method presented is applicable with high accuracy in the range 0·005–5 mg of water in a large variety of substances.

ИЗУЧЕНИЕ ИОНОИЗБИРАТЕЛЬНЫХ ЭЛЕКТРОДОВ НА ОСНОВЕ СУЛЬФИДА МЕДИ(II):

Gillis Johansson and Kerstin Edström, *Talanta*, 1972, **19**, 1623.

Резюме—Измерены изменения потенциала жидкостного спая при использовании различных электродов сравнения в растворах меди(II). Наклон и отрезок калибровочной кривой избирательного для меди электрода зависит от отбора электрода сравнения. Состояние поверхности избирательного для меди электрода марки Орион испытано микроскопическим путем и рассмотрено влияние окислительно-восстановительного потенциала на коррозионную устойчивость электрода. Окисляющие растворы вызывают оброзование язв при дислокациях в материале и появление смешанного напряжения электрода. Наклон, устойчивость и скорость ответа значительно ниже в случае присутствия язв на поверхности электрода. Показано что полирование алмазами в значительной мере улучшает характеристики электрода.

КОСВЕННОЕ ОПРЕДЕЛЕНИЕ МИКРОГРАММОВЫХ КОЛИЧЕСТВ МЫШЬЯКА МЕТОДОМ АТОМНО-АБСОРБЦИОННОЙ СПЕКТРСКОПИИ, ПУТЕМ СЖИГАНИЯ ЭКСТРАКТА МЫШЬЯКОВОМОЛИБДЕНОВОЙ КИСЛОТЫ В МИБК:

Y. Yamamoto, T. Kumamaru, Y. Hayashi, M. Kanke and A. Matsui, *Talanta*, 1972, **19**, 1633.

Резюе—Разработано косвенное определение мышьяка методом атомно-абсорбционной спектроскопии. Мышьяк(III) окисляют в мышьяк(V) иодом, затем образуют мышьяковомолибденовую кислоту и её экстрагируют метилизобутилкетоном (МИБК) из 0,2 — 1,6*M* раствора соляной кислоты. Избыток молибдата устраняют из органической фазы и молибден в форме гетерополикислоты определяют на основе его атомного поглощения при 313,3 нм. Силикат и фосфат мешают определению. Описана методика определения частей на миллион мышьяка в воде.

ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ ВОДЫ С КУЛОНОМЕТРИЧЕСКИ ОБРАЗОВАННЫМ РЕАГЕНТОМ КАРЛА ФИШЕРА:

Ronald Karlsson, *Talanta*, 1972, **19**, 1639.

Резюме—Дальше разработана методика кулонометрического определения небольших количеств воды, описанная в предыдущей стате. Улучшенные электронные цепи и новая конструкция электролитической ячейки позволили протянуть область применимости метода и сокращать продолжительность анализа. Использование подвижной печи приспособленной к ячейке также позволяет определять воду в твердых веществах. Методом можно определять с высокой точностью 0,005–5 мг воды в множестве разных веществ.

Studies on the extraction and determination of metals—I. Extraction of hafnium into methyl isobutyl ketone and tributyl phosphate: Norio Ichinose, *Talanta*, 1972, **19**, 1644. (Department of Chemistry, Faculty of Liberal Arts, Yamaguchi University, Yamaguchi-City, Japan.)

Summary—The effect of various factors on the distribution of hafnium ($<5.60 \times 10^{-4}M$) between different acids and methyl isobutyl ketone (MIBK) or tributyl phosphate (TBP) was studied by using $^{175+181}$Hf as a tracer. When the extraction is made from 7·5–11*M* hydrochloric acid with an equal volume of 1*M* TBP in benzene, hafnium is extracted quantitatively (>99%). The hafnium can be stripped with 1–3*M* hydrochloric acid.

Non-destructive method for the analysis of gold(I) cyanide plating baths. Complexometric determination of nickel and indium: Rudolf Přibil and Vladimír Veselý, *Talanta*, 1972, **19**, 1647. (Laboratory of Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia).

Summary—A method is described for rapid determination of nickel and indium in gold(I) cyanide baths containing large amounts of citric acid and/or sodium citrate, without previous destruction of organic matter. Gold is removed by extraction with ethyl acetate. In one aliquot of the solution indium is masked with thioglycollic acid and nickel is precipitated with sodium diethyldithiocarbamate, extracted into chloroform, stripped into water and determined complexometrically. In a second aliquot indium and nickel are precipitated together with the same reagent and stripped into water, then nickel is masked with 1,10-phenanthroline, and indium is determined by direct titration with EDTA.

Potentiometric argentimetric method for the successive titration of sulphide and dissolved sulphur in polysulphide solutions: Sanae Ikeda, Hiromu Satake, Takeo Hisano and Toshio Terazawa, *Talanta*, 1972, **19**, 1650. (Department of Applied Chemistry, Faculty of Engineering, Tokushima University, Tokushima, Japan.)

Summary—Sulphide sulphur and dissolved sulphur in a polysulphide solution can be successively determined with satisfactory accuracy and reproducibility by potentiometric argentimetry in which a sulphide-selective indicator electrode is used. Before the titration, polysulphide ions need to be converted by an excess of potassium cyanide into thiocyanate and sulphide ions. The excess of cyanide ions is masked with formaldehyde and sulphuric acid, then the solution is made alkaline with ammonia and titrated with silver nitrate till the first end-point is reached (sulphide sulphur). After the acidification of the solution with sulphuric acid, the titration is continued till the second end-point is attained (dissolved sulphur).

ИЗУЧЕНИЕ ЭКСТРАКЦИИ И ОПРЕДЕЛЕНИЯ МЕТАЛЛОВ—I. ЭКСТРАКЦИЯ ГАФНИЯ МЕТИЛИЗОБУТИЛКЕТОНОМ И ТРИБУТИЛФОСФАТОМ:

NORIO ICHINOSE, *Talanta*, 1972, **19**, 1644.

Резюме—Изучено влияние разных факторов на распределение гафния ($<5{,}60 \cdot 10^{-4}M$) между разными кислотами и метилизобутилкетоном (МИБК) или трибутилфосфатом (ТБФ), с использованием $^{175+181}$Hf в качестве индикатора. При экстрагировании из $7{,}5 - 11M$ раствора соляной кислоты с тем же объемом $1M$ ТБФ в бензоле, гафний экстрагируется количественно ($>99\%$). Гафний можно освободить 1–3*M* раствором соляной кислоты.

НЕДЕСТРУКТИВНЫЙ МЕТОД АНАЛИЗА ГАЛЬВАНИЧЕСКОЙ ВАННЫ СОДЕРЖАЩЕЙ ЦИАНИД ЗОЛОТА(I). КОМПЛЕКСОНОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИКЕЛЯ И ИНДИЯ:

R. PRIBIL and V. VESELY, *Talanta*, 1972, **19**, 1647.

Резюме—Описан метод быстрого определения никеля и индия в ваннах цианида золота(I), содержащих большие количества лимонной кислоты и (или цитрата натрия, без предварительного разложения органического вещества. Золото устраняют экстракцией с этилацетатом. В аликвотной части раствора маскируют индий тиогликолевой кислотой и осаждают никель диэтилдитиокарбаминатом натрия, экстрагируют хлороформом, переводят в водный раствор и определяют никель комплексонометрическим методом. В другой аликвотной части раствора индий и никель осаждают одновременно пользуясь тем же реагентом и переводять в водный раствор; никель затем маскируют 1,10-фенантролином а индий определяют непосредственным титрованием с ЭДТА.

ПОТЕНЦИОМЕТРИЧЕСКИЙ АРГЕНТОМЕТРИЧЕСКИЙ МЕТОД ПОСЛЕДОВАТЕЛЬНОГО ТИТРОВАНИЯ СУЛЬФИДА И РАСТВОРЕННОЙ СЕРЫ В РАСТВОРАХ ПОЛИСУЛЬФИДА:

SANAE IKEDA, HIROMU SATAKE, TAKEO HISANO and TOSHIO TERAZAWA, *Talanta*, 1972, **19**, 1650.

Резюме—Метод потенциометрической аргентометрии позволяет определять сульфидную серу и растворенную серу в растворе полисульфида с довольной точностью и воспроизводимостью, пользуясь селективным для сульфидиона индикаторным электродом. Перед титрованием полисульфидионы надо превратить в тиоцианат- и сульфидионы обработкой с избытком цианида калия. Избыток цианидионов маскируют формальдегидом и серной кислотой, раствор затем подщелачивают аммиаком и титруют нитратом серебра до первого конца титрования (сульфидная сера). После подкисления раствора серной кислотой титрование продолжают до второго конца титрования (растворенная сера).

Cation-exchange of metal ions in organic solvent-cupferron media: J. Korkisch and M. M. Khater, *Talanta*, 1972, **19**, 1654 (Analytical Institute, University of Vienna, IX Wahringerstrasse 38, Austria.)

Summary—Distribution coefficients of 20 metal ions were determined on the strongly acidic cation-exchanger Dowex 50 in a 30:7:1 mixture of chloroform–methanol–$1M$ hydrochloric acid which was $0{\cdot}1M$ in cupferron. In this system the distribution coefficients of Fe(III), Ti(IV), Cu(II), Ce(III) and Th are lower by several orders of magnitude than those of Ni, Mn(II), Cd, Co(II), Ca, U(VI), and Sr. It is possible to separate these two groups of elements on an ion-exchange column.

Comparative study of analytical properties and applications of picolinaldehyde thiosemicarbazone and selenosemicarbazone: J. M. Cano Pavon and F. Pino, *Talanta*, 1972, **19**, 1659. (Department of Analytical Chemistry, University of Seville, Seville, Spain.)

Summary—The analytical properties of picolinaldehyde thiosemicarbazone and selenosemicarbazone have been studied, in order to investigate the changes produced when the Se atom is substituted for the S atom. The ionization constants of both substances are very similar. The complexes of picolinaldehyde selenosemicarbazone with cations in aqueous solution are less stable, and the absorption spectra show bathochromic and hypochromic shifts. The introduction of the Se atom offers no advantages in the analytical application of these compounds.

On the nature of so-called "Khimdu": Yong Kuen Lee, Kyu Ja Whang and Keihei Ueno, *Talanta*, 1972, **19**, 1665. (Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan).

Summary—The reagent called "Khimdu" has been investigated and evidence found to show that it is not a pure compound but a mixture of several reaction products.

Zur Frage des Verlustes von Molybdän während der Analyse von metallischem Wolfram auf Molybdänspuren: E. Lassner and H. Schedle, *Talanta*, 1972, **19**, 1670. (Versuchsanstalt, Metallwerk Plansee A. G., A-6600 Reutte, Austria.)

Summary—It is shown that oxidative annealing of metallic tungsten to tungsten trioxide causes a decrease in the molybdenum content. Thus such annealing must be avoided when the molybdenum content is to be determined. On the other hand, when the tungsten is dissolved in a mixture of hydrofluoric and nitric acids with subsequent fuming with sulphuric acid, no such decrease in the molybdenum content takes place.

КАТИОННЫЙ ОБМЕН ИОНОВ МЕТАЛЛОВ В СРЕДАХ СОДЕРЖАЩИХ ОРГАНИЧЕСКИЕ РАСТВОРИТЕЛИ И КУПФЕРРОН:

J. Korkisch and M. M. Khater, *Talanta*, 1972, **19**, 1654.

Резюме—Определены коэффициенты распределения 20 ионов металлов на сильнокислом катионообменнике Дауекс 50 в смеси хлороформа, метанола и 1*M* соляной кислоты 30:7:I, в присутствии 0,1*M* купферрона. В этой системе коэффициенты распределения Fe(III), Ti(IV), Cu(II), Ce(III) и Th в несколько раз ниже чем коэффициенты распределения Ni, Mn(II), Cd, Co(II), Ca, U(VI) и Sr. Поэтому удается разделять эти две группы элементов на колонке ионообменника.

СРАВНЕНИЕ ПРИМЕНИМОСТИ В АНАЛИЗЕ ТИОСЕМИКАРБАЗОНА И СЕЛЕНОСЕМИКАРБАЗОНА ПИКОЛИНАЛЬДЕГИДА:

J. M. Cano Pavon and F. Pino, *Talanta*, 1972, **19**, 1659.

Резюме—Изучены аналитические характеристики тиосемикарбазона и селеносемикарбазона пиколинальдегида с целью определить эффект замещения атома серы атомом селена. Константы ионизации обоих веществ очень похожие. Комплексы селеносемикарбазона пиколинальдегида с катионами в водном растворе менее устойчивы, а спектры светопоглощения показывают батохромные и гипсохромные перемещения. Введением атома селена не получаются преимущества в применении этих соединений в анализе.

ПРИРОДА ТАК НАЗЫВАЕМОГО "КХИМДУ":

Yong Kuen Lee, Kyu Ja Whang and Keihei Ueno, *Talanta*, 1972, **19**, 1665.

Резюме—Результаты изучения так называемого "Кхимду" показывают что это вещество не представляет собой чистое соединение, но ряд продуктов реакции.

К ВОПРОСЕ ПОТЕР В МОЛИБДЕНЕ ПРИ ОПРЕДЕЛЕНИИ СЛЕДОВ МОЛИБДЕНА В МЕТАЛЛИЧЕСКОМ ВОЛЬФРАМЕ:

E. Lassner and H. Schedle, *Talanta*, 1972, **19**, 1670.

Разюме—Показано что окислительнный отжиг металлического вольфрама в трёхокись вольфрама вызывает снижение содержания молибдена. Таким образом надо избежать отжиг в случае определения молибдена. С другой стороны, потери в молибдене не обнаружены если вольфрам растворен в смеси фтористоводородной и азотной кислот с последующим дымлением серной кислотой.